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Environmental Effects of Western Coal Surface Mining. Part III: The Water Quality of Trout Creek, Colorado

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Part III
The Water Quality of Trout Creek, Colorado

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The impact of the mine spoil drainage on the stream is reflected in the larger quantities of dissolved solids and common ions found at on-stream sites adjacent to and below the mine. For trace elements, the mine operation has no detectable impact on Trout Creek in terms of increasing concentrations of Al, As, Cd, Cr, Cu, Fe, Pb, or Zn. Increases in stream concentrations of Mn and Se due to mine inflow can be inferred from the data. Higher concentrations of As, Fe, Mn, Se, and Zn are found in waters draining mine spoils. In the mine spoils, variations in the concentrations of these elements occur with spoil age; more Mn and Zn occur in older spoils, while higher levels of As, Fe, and Se are found in newer spoils.

Chemical equilibrium calculations indicate that alkaline precipitation processes can maintain the low concentrations of Al, Cd, Cu, Fe, Pb, and Zn. The general alkaline characteristics of western streams and aquifers suggests that such precipitation equilibria will limit the soluble heavy metal concentrations.

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Part III - The Water Quality of Trout Creek, Colorado

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FOREWORD

The appearance of surface coal mines is aesthetically displeasing to many and as a result, conclusions are reached about their environmental impact that are not supportable. This report documents the changes in concentrations of various elements and salts in surface water as a result of surface mining in Colorado. Data has been gathered to show the effect of aging of spoils, changes in ground water quality and effects of various mine practices on surface waters.

Only after objective conclusions from valid data are made can good regulatory decisions be made. Our objective is to find the least environmentally damaging methods to obtain fuel, in this case coal, for our growing energy demands.

Donald I. Mount, Ph.D.
Director
Environmental Research Laboratory-Duluth

ABSTRACT

Water quality parameters have been measured at several on-stream and off-stream sites along Trout Creek, which is recipient of water from coal strip-mining operations. Levels of the gross parameters (e.g., specific conductivity), the common ions (e.g., calcium and sulfate), and some trace components (e.g., selenium) are highest in mine spoil drainages.

The impact of the mine spoil drainage on the stream is reflected in the larger quantities of dissolved solids and common ions found at on-stream sites adjacent to and below the mine. For trace elements, the mine operation has no detectable impact on Trout Creek in terms of increasing concentrations of Al, As, Cd, Cr, Cu, Fe, Pb, or Zn. Increases in stream concentrations of Mn and Se due to mine inflow can be inferred from the data. Higher concentrations of As, Fe, Mn, Se, and Zn are found in waters draining mine spoils. In the mine spoils, variations in the concentrations of these elements occur with spoil age; more Mn and Zn occur in older spoils, while higher levels of As, Fe, and Se are found in newer spoils.

Chemical equilibrium calculations indicate that alkaline precipitation processes can maintain the low concentrations of Al, Cd, Cu, Fe, Pb, and Zn. The general alkaline characteristics of western streams and aquifers suggests that such precipitation equilibria will limit the soluble heavy metal concentrations.

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SECTION I

INTRODUCTION

The overall objective of the present investigation has been to provide predictive information regarding the potential effects of western strip coal mining on surface water quality and the concomitant impacts on the aquatic biota. Major subobjectives have included the establishment of data bases for evaluating the potential impact of coal extraction on fresh water resources and ecosystems, the use of chemistry and biology field studies to assess the nature and extent of effects on aquatic ecosystems, and the determination of acute and chronic toxicity and bioaccumulation of contaminants involved. The general research plan has consequently embodied: the chemical characterization of effluents from coal mining sites, evaluation of the impacts of these effluents on surface water quality, and the identification of known and potential toxicants resulting from mining operations. In addition, evaluation of the mechanistic parameters which define the routes of transfer and control the rates and amounts of transfer of toxicants between the mine source(s) and surface waters has been considered.

To accomplish these objectives, field studies dealing with the chemical characteristics of surface water and groundwater associated with a coal mining site have been carried out over a period in excess of two years. These have been coordinated with fish and macroinvertebrate distribution studies at the same site. The fish distribution study results have been summarized by Goettl and Edde (1979) while the macroinvertebrate results have been reported by Canton and Ward (1978). The present report summarizes the water quality impact assessment.

SECTION II

CONCLUSIONS

1. Inflow of surface water and groundwater from the coal mine causes overall decreases in the water quality of Trout Creek. In general, a flow increase of X% between sites above and adjacent to the mine is usually accompanied by an increase in total dissolved solids of 2X% or more. During the spring runoff due to snowmelt at the mine, this situation is exaggerated. A flow increase of Y% between the stream sites above and adjacent to the mine may be accompanied by total dissolved solids increases as high as 50Y%.

2. The increases in dissolved solids observed appear to be dependent on the extent of weathering that the disrupted strata of the mine have undergone. For recently exposed strata, increases in sodium, alkalinity, and sulfate are predominant. For strata which have been exposed longer, calcium, magnesium, alkalinity, and sulfate concentrations predominate. Consequently, exposure of the strata results in water quality decreases which are initially influenced by dissolution of sodium salts; when these are depleted, the less soluble calcium and magnesium salts control the equilibria. The latter are thus responsible for the long-term effects on water quality.

3. Spatial and temporal variations in the dissolved solids, specific conductivity, hardness, calcium, magnesium, sodium, potassium, sulfate, and chloride all exhibit the same pattern as the recipient stream progresses past the mine. Levels are lowest at sites above all mining, increase to maxima at sites of maximum inflow from the mine, and decline at sites downstream of the mine. The highest impacts on the water quality occur during the spring snowmelt at the mine elevation.

4. The mine operation has no detectable impacts on Trout Creek in terms of significant increases in the concentrations of Al, As, Cd, Cu, Fe, Pb, and Zn.

5. Significant increases in the stream concentrations of Mn and Se due to the mine inflow can be inferred from the data. Although these increases occur, their magnitudes are such that significance in terms of potential impacts on aquatic biota does not appear likely. Exception to this may occur at a mine pond draining an exposed cut.

6. In terms of the groundwater impacts, higher concentrations of several elements, e.g., Fe, Mn, and Zn, are associated with subsurface waters in equilibrium with the oldest spoils. The reverse appears true for Cd, Cr, and Cu but the data are much more limited. Higher levels of As, Hg, and Se are associated with groundwater in equilibrium with the less weathered spoils.

7. Chemical equilibrium calculations indicate that the concentrations of Al, Cd, Cu, Fe, Pb, and Zn can be maintained at or below the levels observed by precipitation processes. These are largely hydroxide and/or carbonate precipitation reactions. The concentrations of these precipitants are influenced by the mine operation such that maintenance of these controlling equilibria may be very long-term. The generally basic and alkaline characteristics of western streams and aquifers, coupled with the fairly universal influx of alkaline constituents from most western coal mine operations, suggest that such precipitation equilibria will limit possible heavy metal impacts in the western coal development region.

8. Water quality conditions, specifically characteristic of the Trout Creek site and generally characteristic of the western coal development area, allow the prediction of the principal soluble forms of heavy metals via chemical equilibrium evaluations. The primary soluble forms are expected to be either a simple aquated form (e.g., $Zn^{+2}(aq)$) or a hydrolyzed form (e.g., $Fe(OH)_2^{+}$). For some elements (e.g., Cu), soluble complexes involving carbonate may also be important. At sites where the sulfate levels exceed approximately 400-500 mg/liter, the solubilities of Mn, Pb, and Zn may be enhanced due to the formation of sulfate complexes.

SECTION III

RECOMMENDATIONS

The data collected during the study period show a significant increase in total dissolved solids in the mine area. By comparing the sites which reflect runoff from recontoured spoils to those which remain ungraded, it is apparent that returning the spoils to their original contour reduces the extent of percolation through the spoils and consequently the impact on water quality. It is therefore recommended that leveling take place as quickly as possible after the mining operations are completed. Revegetation of these recontoured spoils will further prevent percolation and subsequent erosion.

It is also recommended that a vegetated buffer zone between recipient stream and associated mining operations be maintained. Such undisturbed areas serve to further reduce the impact of mine drainage on recipient streams.

SECTION IV

SITE SELECTION

Several factors were considered in the selection of the study site. The Edna Coal Mine and the recipient stream, Trout Creek, were chosen for study on the following bases. The mine operation is such that a gradation of aged (weathered) to new spoils could impact the stream as it progresses along the mine. Groundwater and surface water hydrology as well as a reasonable amount of chemical data were available. The stream originates in a pristine area immediately above the mine such that reference point (baseline) measurements could be made. Finally, the mining activities were likely to be the principal cause of any water quality and aquatic biology changes observed.

DESCRIPTION OF THE STUDY AREA

The area has been previously described by McWhorter *et al.* (1975). The description has been summarized here for the convenience of the reader.

Physical Characteristics

The area has been described by Bass *et al.* (1955). It lies in northwestern Colorado in the southeastern portion of a gently rolling, 2,590 km^2, coal mining region known to the industry as the eastern part of the Yampa coal field. The climate is semiarid with an annual precipitation of 38 to 51 cm; at least half of this occurs as snow.

Trout Creek is west of the town of Oak Creek and southwest of Steamboat Springs (Figure 1). It originates in a mountain region at an elevation in excess of 3550 m, runs several kilometers through national forest, enters a small valley containing Pittsburgh and Midway's Edna Mine, and continues northward to its confluence with the Yampa River near Milner, Colorado. At the higher elevations above the mine, the land is largely vegetated with trees and native grasses. In the valley, vegetation changes to native grasses and some alfalfa fields. Stock ranches utilize the land across the creek and downstream from the mine.

It may be noted in Figure 1 that mining started on the upstream side in the World War II era. Although the strata disrupted by mining in the older area have not been regraded to their original aspect, the area is sparsely vegetated in native scrubbrush (oak) and grasses. Mining operations then moved progressively north, reaching the northern extreme around 1970; these latter were the first spoils to be regraded to the original contours and are

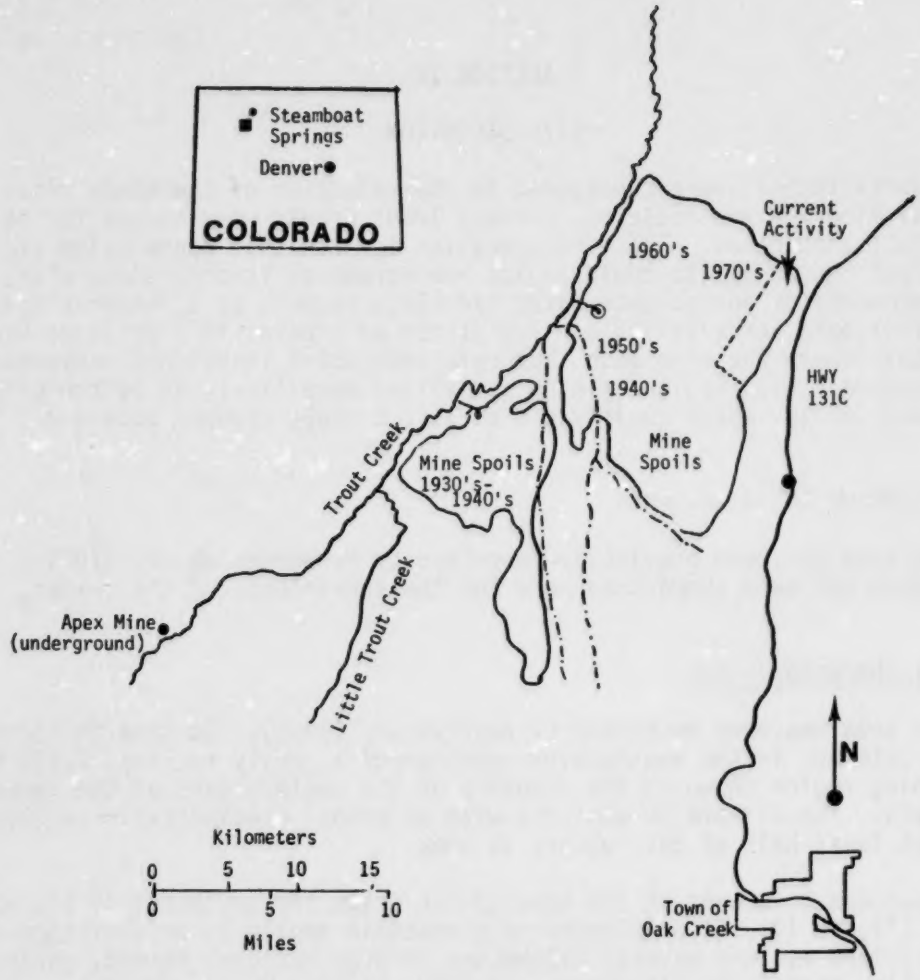

Figure 1. Location map of the mine study site. Inset indicates location in Colorado.

now partially vegetated with native plants. Current activity is centered on the upslope (east) side of the mine near the top of the ridge separating the Oak and Trout Creek watersheds.

The area mined during the 1950's includes a bowl-shaped cut, about 200 m^2 × 30 m deep, near the base of the spoils that is barren of vegetation. With this exception, the density of native vegetation is approximately proportional to the age of the spoil material.

A cross-sectional diagram of the slope after mining is given in Figure 2. The mine slopes to the creek at approximately 10°. The surface material is composed largely of mine overburden which is the only soil layer above bedrock. Below the surface, which is graded only in the northern end of the mine, the overburden consists of debris ranging in size from that associated with clays to rocks 1 m in diameter. This material normally ranges from 10 to 20 m in depth and represents a marked contrast to the relatively well-sorted soils and strata present prior to mining. The mine is typically separated from the creek by approximately 50 m of undisturbed area which serves to some extent as a buffer zone through which mine drainage must pass.

Geology

The geology of the site has been summarized by Campbell (1923) (see Figure 3). This indicates that the Trout Creek and Little Trout Creek watersheds above the mine are principally of the Iles formation. The mine portion of the area and downstream from it are of the Williams Fork formation. Thus, the groundwater input above the mine represents an equilibrium situation reflective of a different geological formation than that directly associated with the mine.

The strata included in the above formations are depicted in Figure 4. In the study area, the sandstone member immediately above the Williams Fork formation has been eroded away. The remaining strata lies on a 10° slope toward the creek (Figure 2). However, several of the strata contained in the Iles and the Williams Fork formations are similar, and both contain shale, sandy shale, and limy shale (Figure 4). Differences in terms of depths and proportions of these strata within the Iles and the Williams Fork formations could account for differences in groundwater characteristics associated with these two formations; these differences are not expected to be large.

The coal deposits associated with the Williams Fork formation at the mine are of the middle coal group; the Lennox and Wadge seams have been mined most extensively. These coals have ash contents between 5% and 9% and sulfur levels ranging from 0.5% to 3% (see Table 1).

Soils in the undisturbed areas are generally poorly developed; bedrock frequently occurs within 1 m of the surface and is overlain by a layer of clay. These two factors limit the penetration of precipitation into the underlying strata in undisturbed areas; mining makes the strata accessible to a much higher degree (Goettl and Edde 1979).

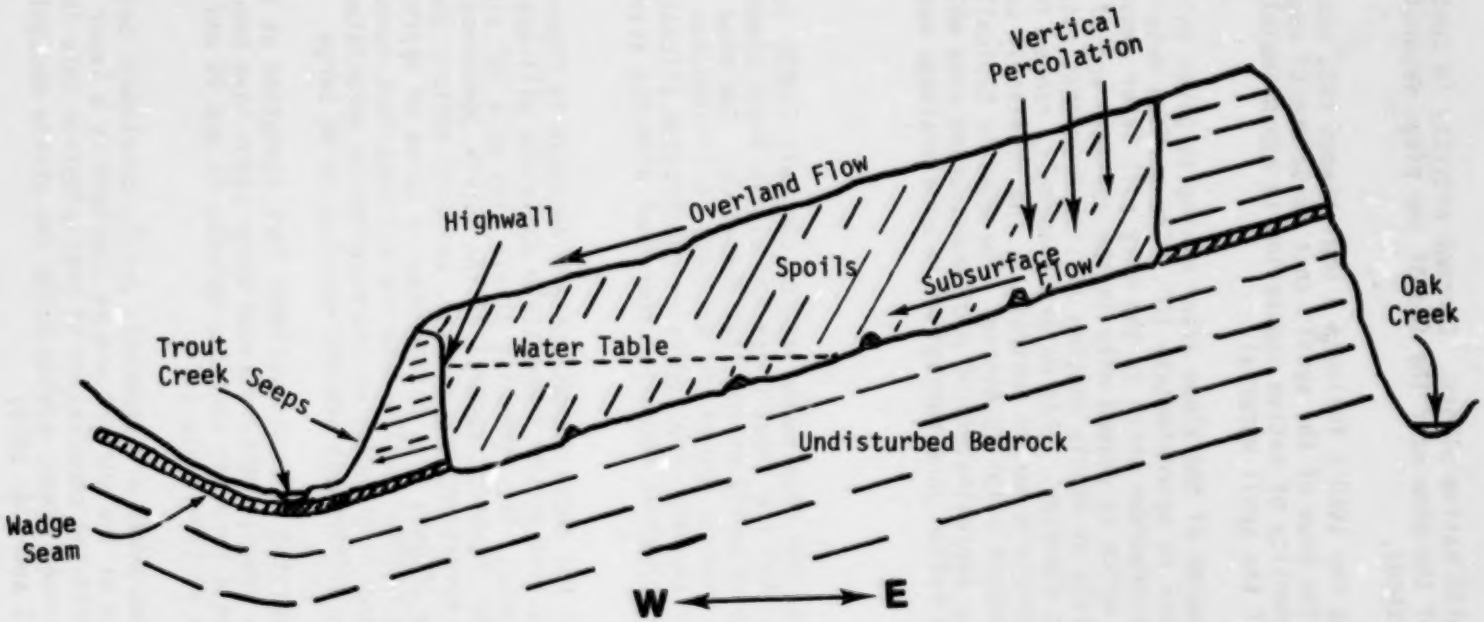

Figure 2. Schematic east-west cross-section near station C6 (taken from report by McWhorter *et al.* 1975).

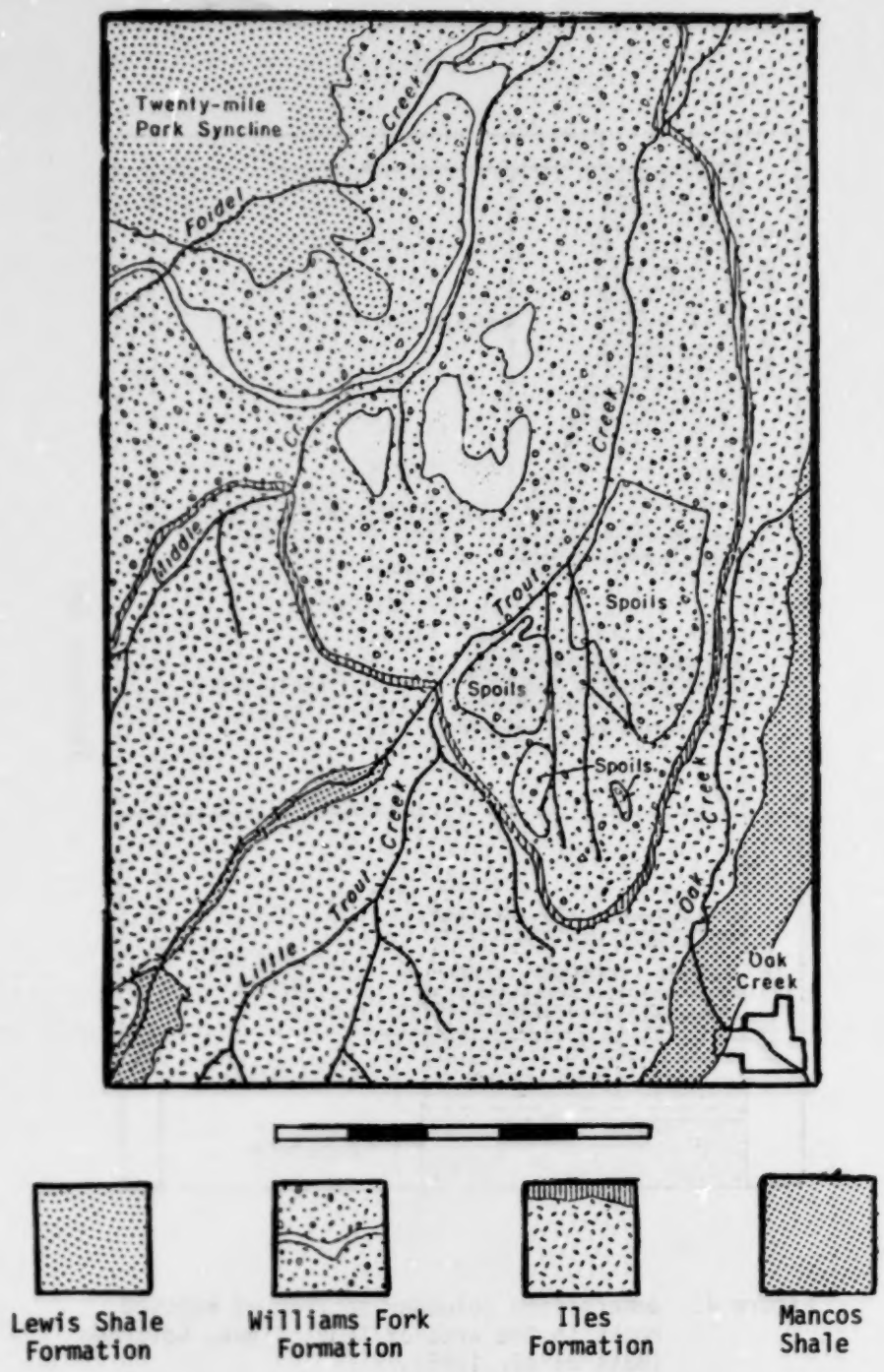

Figure 3. Geologic map of the Edna Mine and surrounding area (McWhorter *et al.* 1975).

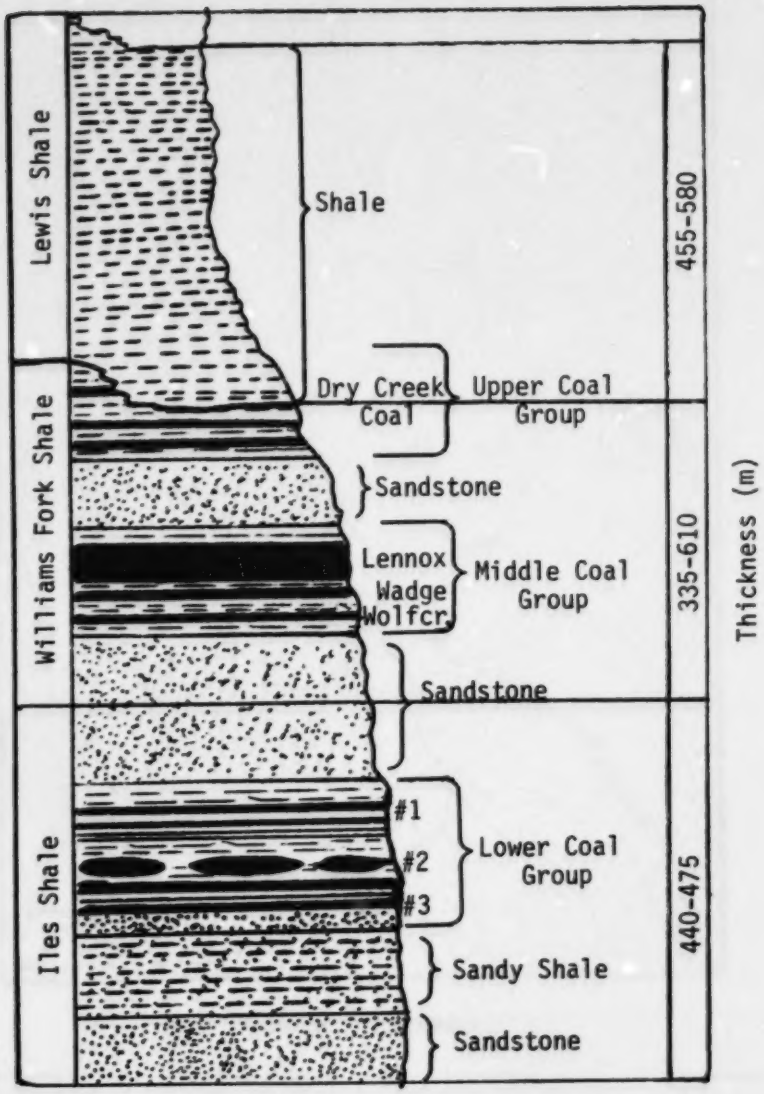

Figure 4. Generalized columnar section of exposed rocks in the area of Trout Creek, Colorado (Bass *et al.* 1955).

TABLE 1. ANALYSES OF COAL SAMPLES FROM THE EDNA MINE[a/] (A = AS RECEIVED, B = AIR DRIED, C = MOISTURE-FREE, D = MOISTURE AND ASH-FREE)

Mine and location	Formation	Air-drying loss	Form of analysis	Proximate			Ultimate						Heating values	
				Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Hydrogen	Carbon	Nitrogen	Oxygen	Calories	BTU
Edna strip mine, Edna Coal Co., SE¼ sec. 24, T. 4 N., R. 86 W.	Williams Fork	5.3	A	11.0	36.5	47.7	4.8	0.5	5.9	65.8	1.3	21.7	--	11,640
			B	6.0	38.6	50.3	5.1	0.5	5.6	69.5	1.4	17.9	--	12,290
			C	--	41.0	53.6	5.4	0.6	5.2	73.9	1.5	13.4	--	13,070
			D	--	43.4	56.6	--	0.6	5.5	78.1	1.5	14.3	--	13,820
Edna strip mine, Edna Coal Co., SE¼ sec. 24, T. 4 N., R. 86 W.	Williams Fork	1.7	A	10.1	36.4	47.1	6.4	0.6	5.8	65.0	1.4	20.8	--	11,400
			B	8.5	37.1	47.9	6.5	0.7	5.7	66.1	1.5	19.5	--	11,600
			C	--	40.5	52.4	7.1	0.7	5.2	72.3	1.6	13.1	--	12,670
			D	--	43.6	56.4	--	0.8	5.6	77.8	1.7	14.1	--	13,640
Edna strip mine, Edna Coal Co., SE¼ sec. 24, T. 4 N., R. 86 W.	Williams Fork	5.2	A	9.9	39.9	46.2	4.0	2.5	--	--	--	--	--	--
			B	5.0	42.1	48.6	4.3	2.6	--	--	--	--	--	--
			C	--	44.3	51.2	4.5	2.9	--	--	--	--	--	--
			D	--	46.4	53.6	--	--	--	--	--	--	--	--
Arthur mine (later known as Edna) of John Arthur SW¼ sec. 24, T. 4 N., R. 86 W.	Williams Fork	2.7	A	10.1	38.4	43.5	8.0	0.6	5.9	63.0	1.4	21.1	6,228	11,210
			B	7.5	39.5	44.8	8.2	0.7	5.7	64.7	1.5	19.2	6,400	11,520
			C	--	42.7	48.4	8.9	0.7	5.3	70.0	1.6	13.5	6,922	12,460
			D	--	46.9	53.1	--	0.8	5.8	76.8	1.8	14.8	7,600	13,680

[a/] From Bass *et al.* (1955).

Hydrology

Trout Creek is the major drainage of the 110 km^2 watershed which includes the mine. The hydrology of this drainage has been characterized by McWhorter *et al.* (1975). The mean annual discharge measured just below the mine has been estimated at 2.8×10^7 m^3/yr. This is approximately equivalent to a precipitation of 26 cm/yr over the watershed (McWhorter *et al.* 1975). The surface water divides in the area coincide generally with the topographic highs. In the spoil areas, the surface drainage patterns are disrupted in several areas such that precipitation tends to accumulate in depressions and infiltrate into spoils with little or no overland flow. Thus, a high fraction of the precipitation is lost by evapotranspiration or infiltration into the ground. It is clear that mining has changed the surface and subsurface drainage patterns; this can be inferred from Figure 2. The depth to which water can percolate has been generally changed from a few meters to more than 15-20 m; this increases the potential for the dissolution of spoil materials by water. Although a highwall of undisturbed rock exists between the mine and the creek, at least a small amount of subsurface flow from the mine through the alluvial aquifers and into the creek occurs (McWhorter *et al.* 1975). The quantity of this underflow is not known. Small drainages enter the creek from the ranch area opposite the mine but their contribution to the total inflow is small. In general, the major inflow contributions to the stream originate on the mined site.

Monitoring Sites

A total of 15 collection stations were established within the Trout Creek watershed. These include:

1. on stream stations above, along, and below the mine;
2. a station on Little Trout Creek at its confluence with Trout Creek which is fed largely by subsurface drainage not associated with mining; and
3. stations on ponds and streams located in the mine proper.

The locations of these stations and the individual watershed boundaries associated with stations within the mine are shown in Figure 5 while a more detailed description is given in Table 2. It should be noted that the watershed boundaries coincide approximately with reasonably well defined stages of the historic progression of the mining activity (see Figure 1).

The following points concerning these sampling stations should be noted.

1. The C1 and C2 sites are above all surface mining activity. It will be shown below that the water quality parameters (WQP) measured at these two sites are indistinguishable. This indicates that the underground mine (Figure 1) located between them has no impact on the stream and that the WQP measurements at C2 serve as reliable references for deduction of impacts which may occur downstream.

TABLE 2. DESCRIPTION OF THE WATER QUALITY SAMPLING STATIONS

Station number and character					Date sampling started	Description
Trout Creek surface water	Little Trout Creek surface water	Intermittent streams in spoils	Mine drainage pools in spoils	Subsurface water drainage		
C1					Oct. 1973	Surface water from Trout Creek above all mining activity and above Apex Mine
C2					Oct. 1973	Surface water from Trout Creek above Edna Mine and Little Trout Creek, but below Apex Mine
	C13				July 1975	Surface water from Little Trout Creek above Edna Mine
			C3		Oct. 1973	Mine drainage from older spoils
		C9			March 1975	Intermittent stream flowing through older spoils
			C10		March 1975	Mine drainage in newer spoils
C4					Oct. 1973	Surface water from Trout Creek below older spoils
			C5		Oct. 1973	Mine drainage from newer spoils
C6					Oct. 1973	Surface water from Trout Creek below newer spoils
				C7	Oct. 1973	Subsurface water entering Trout Creek below newer spoils
C8					Oct. 1973	Surface water from Trout Creek below newer spoils
C11					March 1975	Surface water on Trout Creek 1.6 km north of oil mining activity
C14					July 1975	Surface water on Trout Creek approximately 8 km north of all mining activity

Downstream

2. Station C13 reflects the influence of Little Trout Creek on Trout Creek. Since the former has much lower flow levels, it has little impact on the WQP's observed at C2 and below.

3. Site C3 is water which seeps from a pond within the oldest area of the mine. Since it accumulates groundwater flowing through this area, it reflects the WQP equilibria characteristic of the most weathered spoils.

4. C5, a similar pond in the spoils of the area mined during the 1950's, reflects the aquatic equilibria characteristic of the middle era spoils.

5. A subsurface water seep at the northern extreme is site C7; it reflects the WQP impacts for the most recent spoils.

6. Stations C9 and C10 are located on intermittent streams originating above and flowing through the mined area. These also reflect the impact of spoils on the WQP's. In terms of spoils exposure, C9 compares with C3 while C10 compares with C5.

7. Stream stations C4, C6, and C8 were selected to reflect the following. Site C4 receives input from the C3, C9, and C10 watersheds (Figure 5) and is therefore expected to reflect the impacts of the older mine operations on the WQP's. The C5 watershed impacts on sites C6 and C8.

8. The total impact of the mine operation can be estimated by comparison of WQP data at C8 with that at C2.

9. The effects of agricultural activities can be deduced by comparing WQP data at C14 with those for C8 or C11.

These delineations are taken into account in the evaluations summarized in succeeding sections.

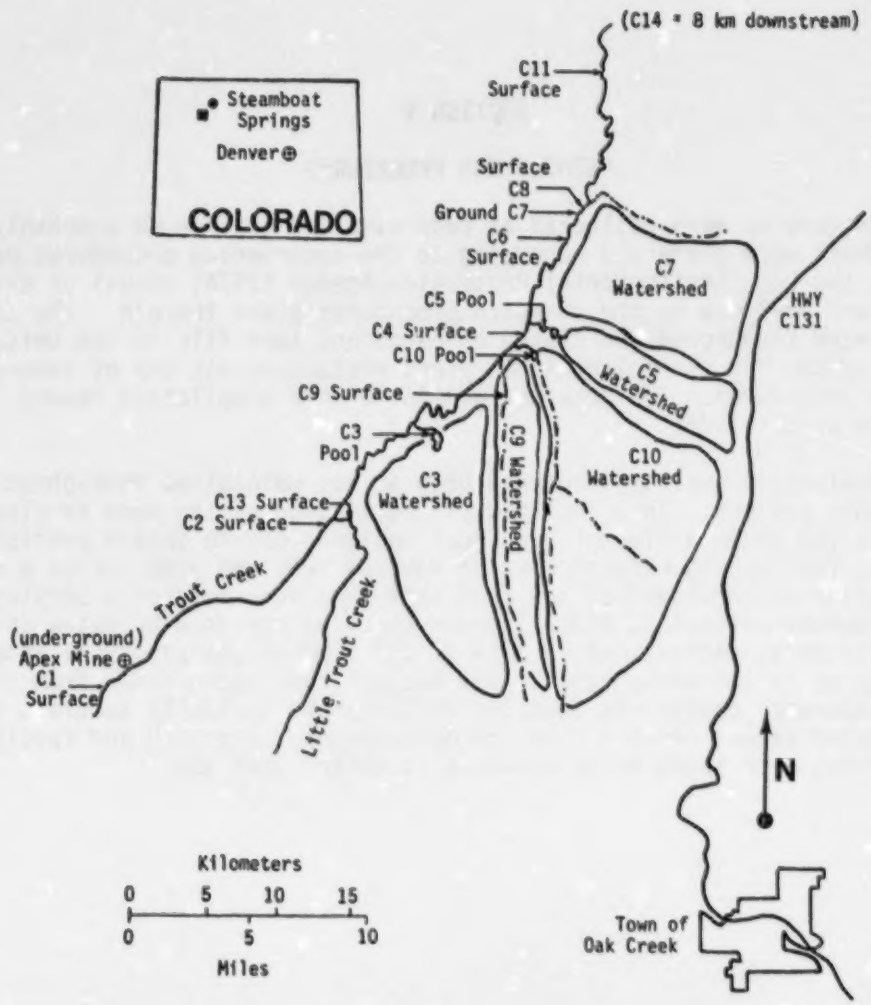

Figure 5. Location map of water quality monitoring stations and mine surface watersheds in the study area. (See Table 2 for more complete description.)

SECTION V

METHODS AND PROCEDURES

Water samples were collected at each sampling station on a monthly basis. These were preserved according to the recommended procedures described by the U.S. Environmental Protection Agency (1974) manual on water analysis and analyzed by the standard procedures given therein. The data obtained were keypunched and placed on permanent tape file in the university computer system for convenient summary and evaluation via any of several available procedures. The data are available in a compilation report (Skogerboe *et al.* 1978).

An analytical quality assurance program was maintained throughout the term of this project. This included (1) submission of the same samples to the analytical lab under different numerical designations to obtain precision estimates, (2) running reference water samples from the USGS (using a designation system which disguised the fact that they were reference samples) to obtain accuracy estimates, and (3) cross checking analyses by using spike-recovery methods. Approximately 3-4% of all samples analyzed were actually check samples of the above types. The overall conclusion drawn from these quality assurance checks was that the analyses are typically accurate to ±10% of the stated value; certain types of measurements, e.g., pH and specific conductivity, were found to be accurate to better than ±5%.

SECTION VI

RESULTS AND DISCUSSION

STREAM DISCHARGE PATTERNS

A plot of typical stream discharge results, obtained from McWhorter *et al.* (1975), is given in Figure 6. In general, flow increased sharply in April/May due to snowmelt, peaked in mid-June, and decreased sharply to its low flow level by mid-July. Maximum flow (mid-June) did not coincide with maximum snowmelt at the mine. The typically 3- to 6-week time lag between these two events reflects the fact that stream flow is influenced by the later snowmelt at the higher elevations on Trout Creek. The influence of this delayed snowmelt flow from higher elevations not associated with mining is one of diluting the overall impact of the higher level of groundwater flow from the mine during this period (see discussion below). The flow pattern shown in Figure 6 varies in magnitude and in time from year to year depending on snowfall and the temperature regime; the trends of the pattern are qualitatively similar each year.

Most of the surface and subsurface inflow from the mine occurs in the distance between stations C2 and C6. Therefore, the differences in discharge at these two sites are indicative of the extent of such mine-associated inflow for any month. Data of this nature indicate that the total flow increases by 20-100% between these two stations depending on the season and runoff conditions. These flow increases due to inflow from the mine are usually accompanied by overall decreases in water quality. It is difficult to generalize but examination of flow and dissolved solids data suggests that a flow increase of X% between C2 and C6 is usually accompanied by an increase in dissolved solids in excess of 2X%. Impacts of this nature, due to the mine operation, are discussed further below.

WATER QUALITY DIFFERENCES WITHIN THE MINE

As previously noted, sites C3, C5, and C7 involve seepage (subsurface) water within various mine watersheds which should reflect differences in the age (weathering) of the spoils. The specific conductivity (SC) reflects gross differences in waters associated with the respective sites. The plot of SC versus time at each site (Figure 7) indicates temporal parallels but distinct and consistent differences in the total dissolved solids concentrations. Of primary interest is that increasing dissolved solids concentrations are associated with progressively more recent mine spoils. Further insight into this may be obtained via examination of the water quality data at each site (averaged over the time period of Figure 7) given in Table 3.

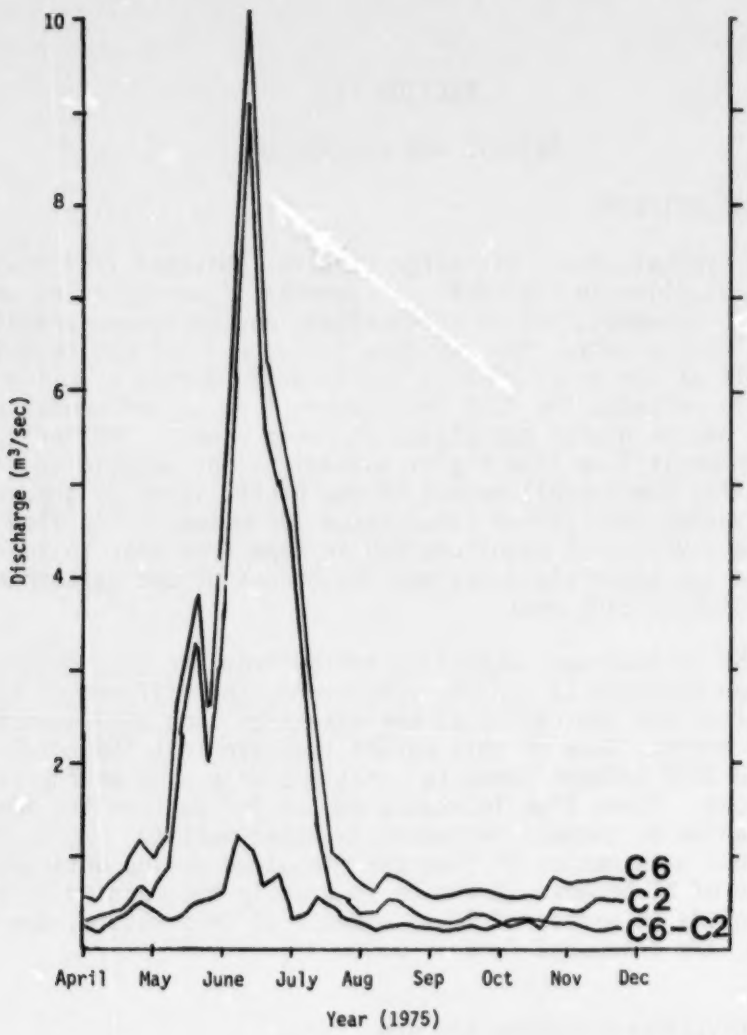

Figure 6. Typical stream discharge data at Trout Creek. (C2 = discharge at on-stream site above mine; C6 = discharge at on-stream site adjacent to mine; C6-C2 = increase in discharge between sites C2 and C6.)

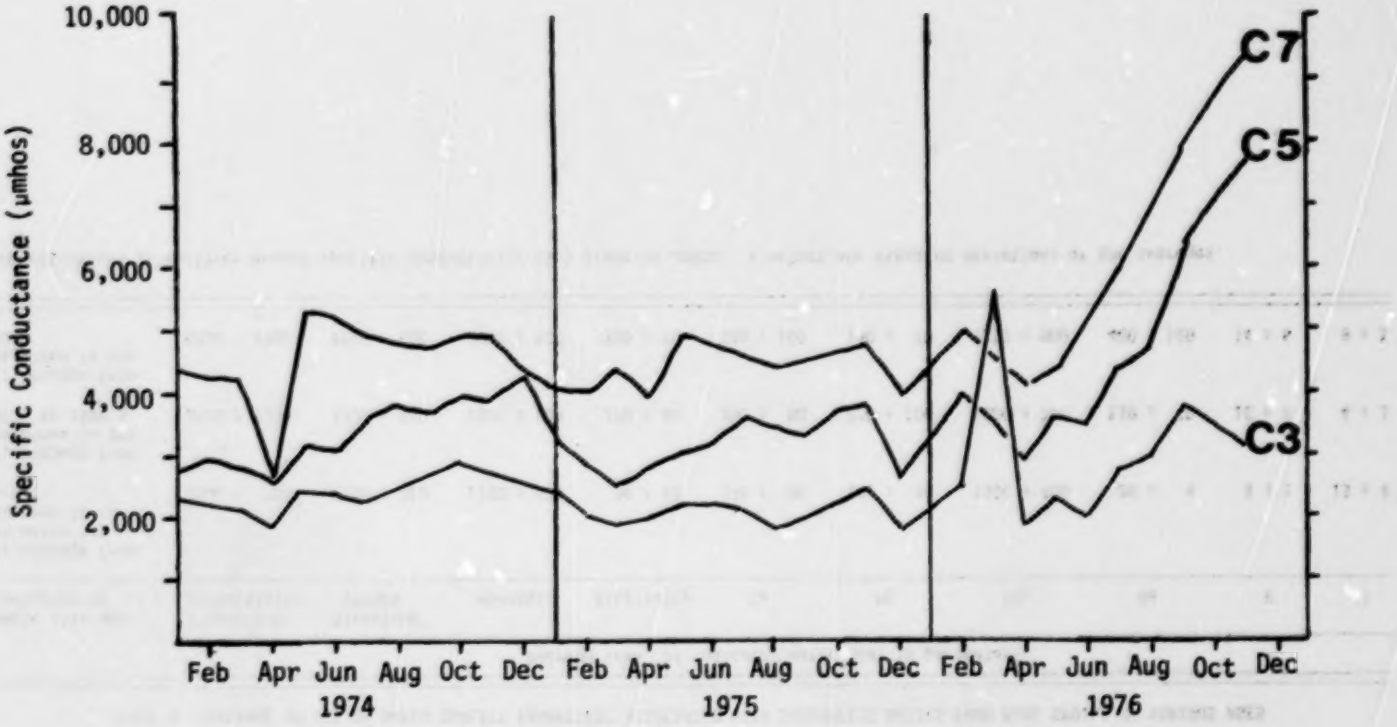

Figure 7. Specific conductivity of surface waters at sites associated with various stages of spoil weathering (C3 spoils approximately 30-40 years old; C5 spoils approximately 15-25 years old; C7 spoils 1-10 years old).

TABLE 3. AVERAGE VALUES OF WATER QUALITY PARAMETERS ASSOCIATED WITH SUBSURFACE WATERS FROM MINE SPOILS OF VARIOUS AGES

Sample site and description	Average level of indicated water quality parameter[a]									
	Specific conductivity	Dissolved solids	Hardness	Alkalinity	Ca	Mg	SO_4	Na	K	Cl
Increasing weathering exposure → C-3; seepage from area which has weathered 30-40 years	2500 ± 700	2100 ± 260	1700 ± 600	94 ± 40	370 ± 80	140 ± 40	1300 ± 400	20 ± 4	4 ± 1	13 ± 4
C-5; seepage from area mined in the 1950's to 1960's	3600 ± 1000	3300 ± 460	2400 ± 800	170 ± 40	350 ± 80	270 ± 100	1800 ± 700	110 ± 40	16 ± 7	4 ± 1
C-7; seepage from area mined in the 1970's	4800 ± 1300	4000 ± 500	2000 ± 500	380 ± 70	320 ± 100	190 ± 70	1300 ± 900	480 ± 120	14 ± 6	8 ± 1

[a] All concentrations in mg/liter except specific conductivity (SC) given in μmhos.; ± values are standard deviations of the averages.

Clearly, the dissolved solids levels increase with decreasing age of the spoils and the same trend is evidenced for alkalinity (HCO_3^-) and sodium. The trend is nearly the opposite for Ca, Mg, and sulfate. This qualitatively suggests the predominant influx of soluble sodium salts (e.g., $NaHCO_3$ and Na_2CO_3) during the early years of water action on the spoils. Ultimately, the more soluble materials of this nature are depleted and the dissolution of less soluble materials (e.g., $CaSO_4$ and $MgSO_4$) becomes predominant. Thus, the exact nature of the impact(s) of such mine effluent waters on surface water quality will ultimately depend on the degree of previous weathering exposure of the spoils, their general mineralogical makeup, and the hydrologic features of the mine area. McWhorter *et al.* (1975) have approximated that the groundwater associated with the Edna Mine will maintain low quality (comparable to that indicated in Table 3) for 500-600 years. There are sufficient amounts of soluble materials in the disrupted areas exposed to water to supply high levels of Ca, Mg, and SO_4 (in particular) over this extended time period.

STREAM WATER QUALITY; GROSS PARAMETERS AND COMMON ION IMPACTS

An overview of WQP changes on spatial as well as temporal bases may be obtained from the specific conductivity data summarized in Figure 8. These data emphasize that the total dissolved solids level at the C2 station above all mining activity was relatively constant. The data for C6, however, emphasize the high dissolved solids influx which occurs during periods of snowmelt at the mine. Moreover, when the primary influx of water is from the higher elevations above the mining activity, this results in rapid dilution of dissolved materials that may be influent along the reaches of the mine. Examination of flow data between C2 and C6 during the snowmelt of 1975, for example, indicates a 15-25% increase in flow primarily due to surface and subsurface runoff from the mine. This was accompanied, however, by a more than 500% increase in the dissolved solids levels in the stream. Similar observations may be noted for other snowmelt and precipitation periods; these indicate that the mine operation is responsible for significant inputs of dissolved solids.

Further examination of Figure 8 indicates groupings of time periods over which the water flow and water quality characteristics are relatively constant. Consequently, to summarize the data into more tractable units, the following seasonal groupings have been defined.

1. July to September is a period when surface runoff contributions are minimal, the rate of evapotranspiration is high, and irrigation return flow will be operative.

2. October to December is a period during which there is no irrigation return flow, natural precipitation and snowmelt are low, and the rate of evapotranspiration is minimal. Thus, comparison of these two time periods provides approximations of subsurface contributions in the presence and absence of irrigation return flow.

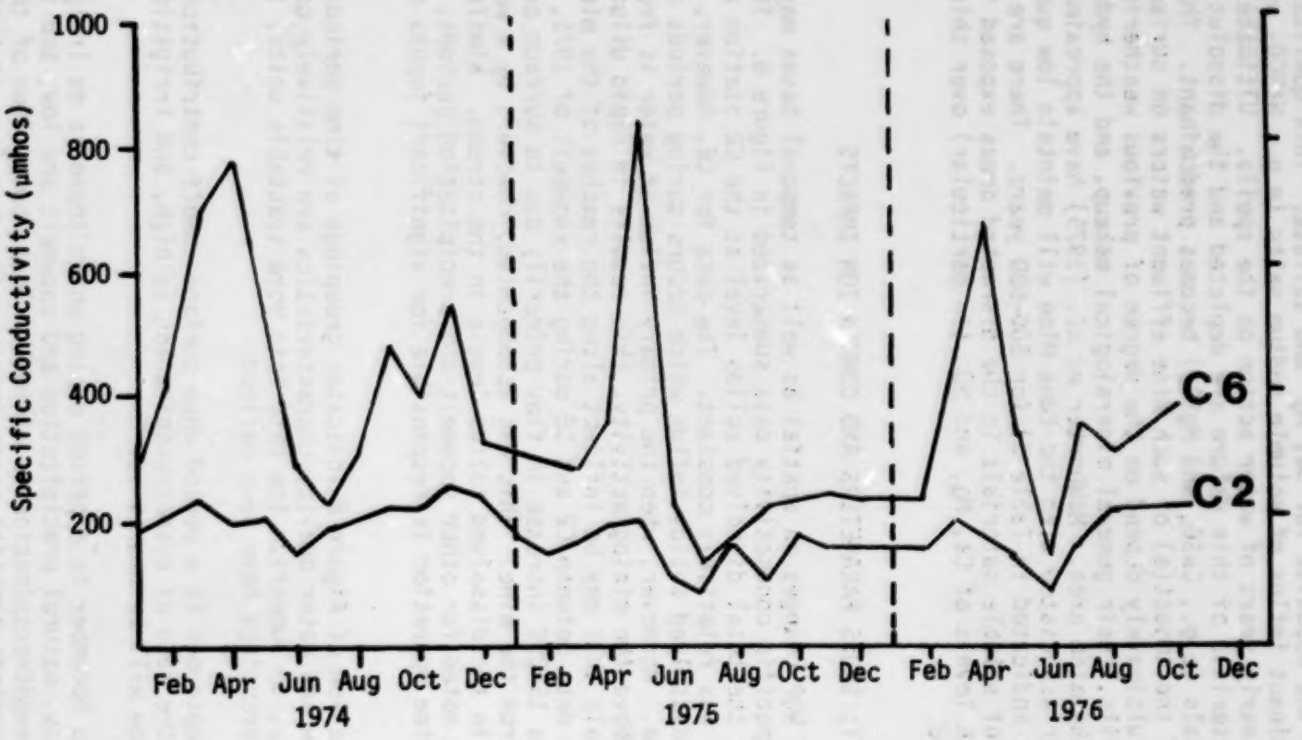

Figure 8. Specific conductivity of surface waters above (C2) and adjacent to the mine (C6).

3. The January to March interval is a reference period during which snowfall and surface, as well as subsurface, contributions should be minimal.

4. April and May coincide in general with maximum snowmelt at the mine elevation and the primary input of dissolved solids.

5. June is segregated due to the high runoff from higher elevations and the concomitant dilution effects discussed above.

The average concentrations of the gross (common) water quality parameters for each of these time blocks have been determined for each sampling station on the stream. These data are presented in the three dimensional plots of Figures 9 through 16. Complete data are published in a summary compilation report (Skogerboe *et al.* 1978). These data can be obtained for the cost of reproduction.

Examination of the dissolved solids data in Figure 9 emphasizes the following distinguishing features.

1. The observed levels at all sites are highest during the April/May snowmelt and lowest during the June snowmelt at higher elevations.

2. The dissolved solids concentration consistently increases in a downstream direction reaching a maximum at approximately the lowest reach of the mine (C8). The general dropoff further downstream is probably due to dilution via other input sources and/or removal of dissolved solids via various processes (e.g., precipitation).

3. The general occurrence of a maximum in the C4 to C6 region with a slight drop thereafter implies (but not conclusively) that the largest dissolved input is associated with the older areas of the mine. Since these areas of the mine have not been regraded to their original contours, infiltration into the spoils is encouraged. Inflow from these areas may consequently be greater.

4. Since all surface drainages from the mined area to the stream occur above C11, the small increase generally occurring between C11 and C14 *may* reflect the effects of irrigation return flow between the two sites.

Examination of similar data plots for hardness, Ca, Mg, SO_4, Na, K, and Cl in Figures 10 through 16, respectively, emphasizes the recurrence of the pattern and associated conclusions discussed above. A further emphasis of the constant nature of this pattern may be obtained by examination of maximum and minimum concentration data for the above parameters in relation to site and season. The lowest concentration of any WQP is consistently observed at sites C1 and C2 above the mine; these reach a minimum value during the high elevation snowmelt of June. The highest WQP concentrations are consistently observed in the April/May snowmelt at the mine and the maximum concentrations usually occur in the stream section immediately adjacent to the mine between C4 and C8.

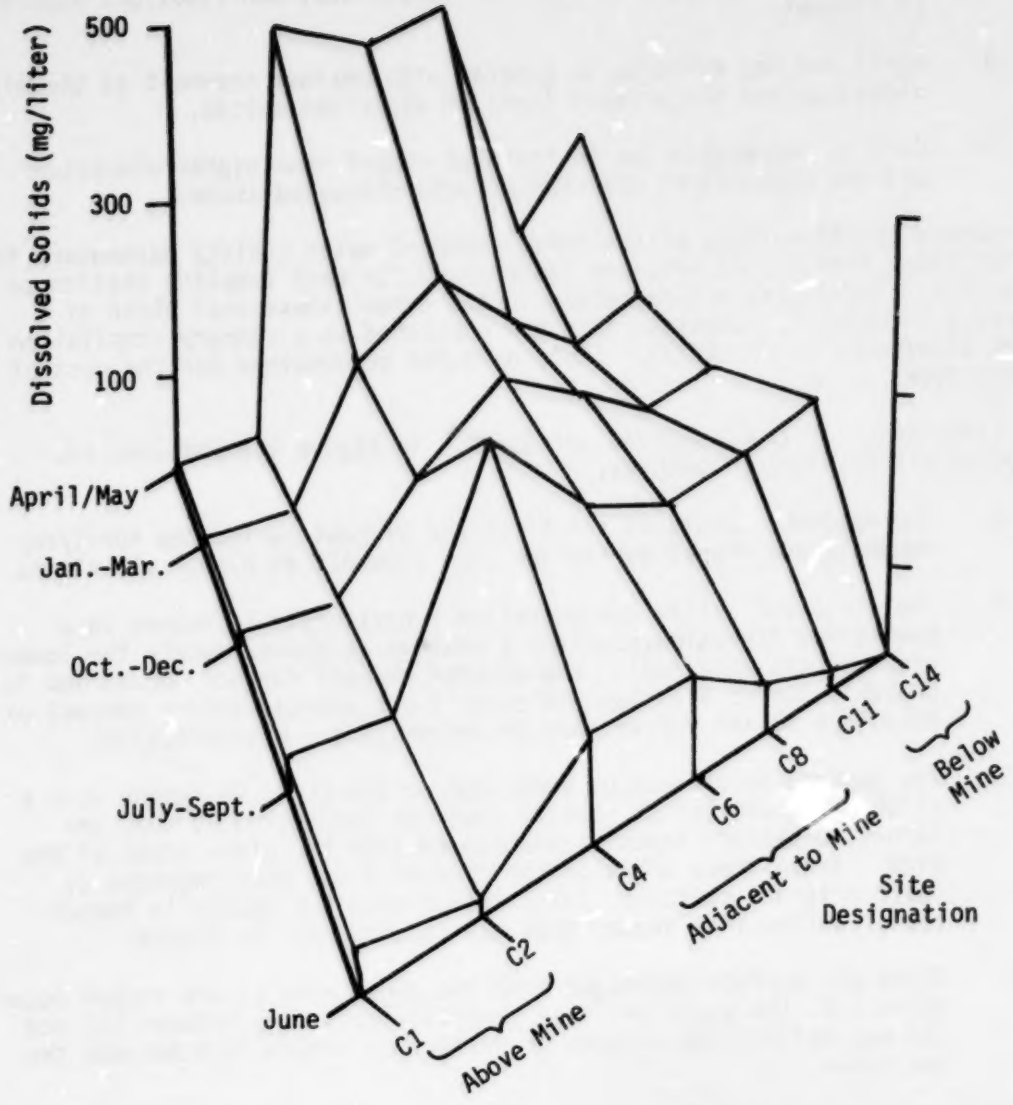

Figure 9. Spatial and temporal distribution of dissolved solids.

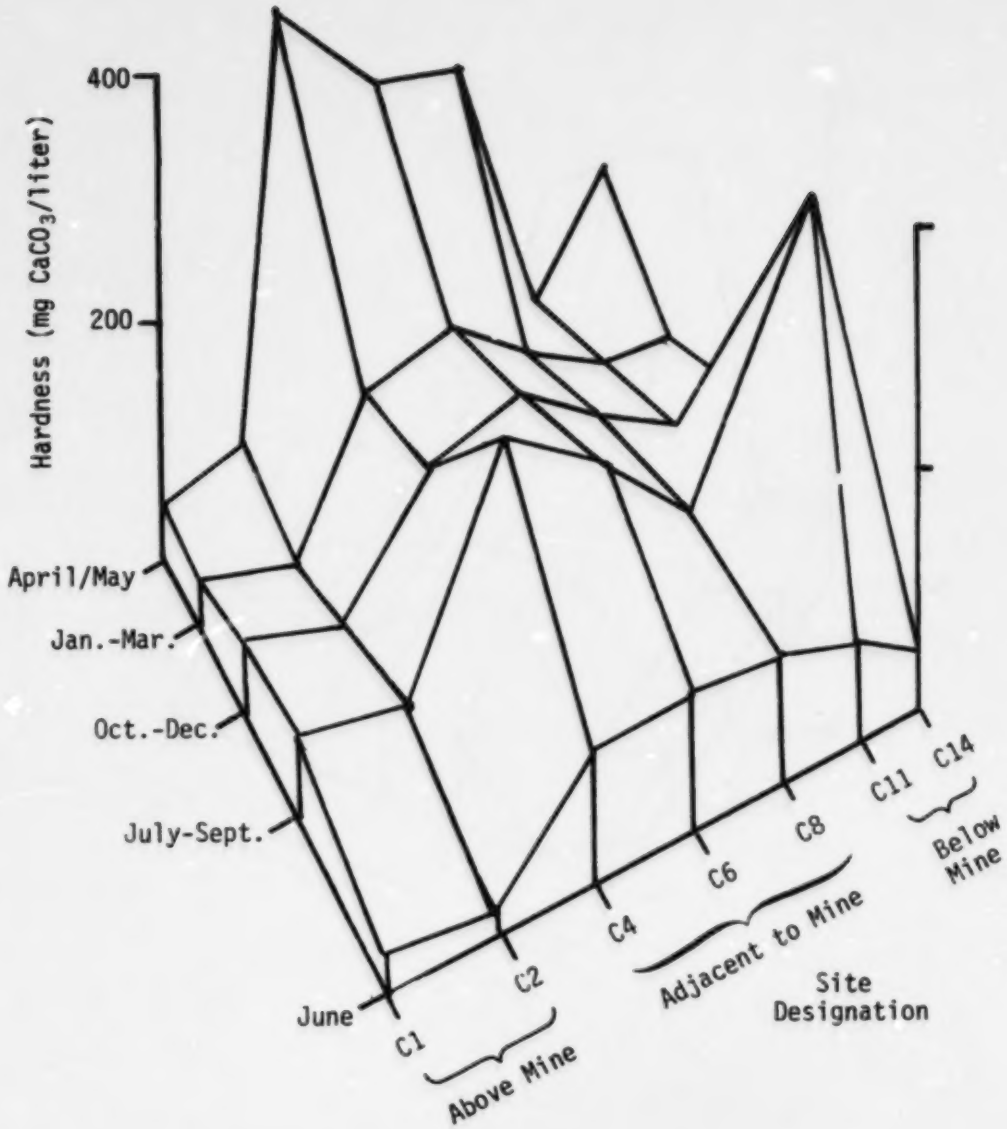

Figure 10. Spatial and temporal distribution of hardness.

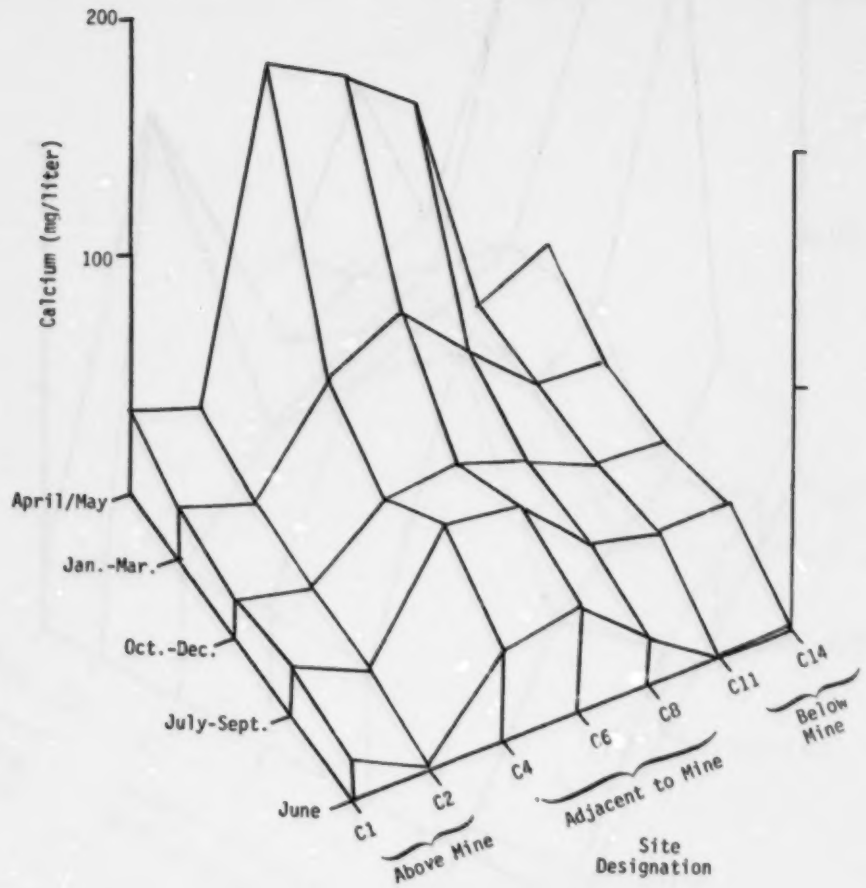

Figure 11. Spatial and temporal distribution of calcium concentrations.

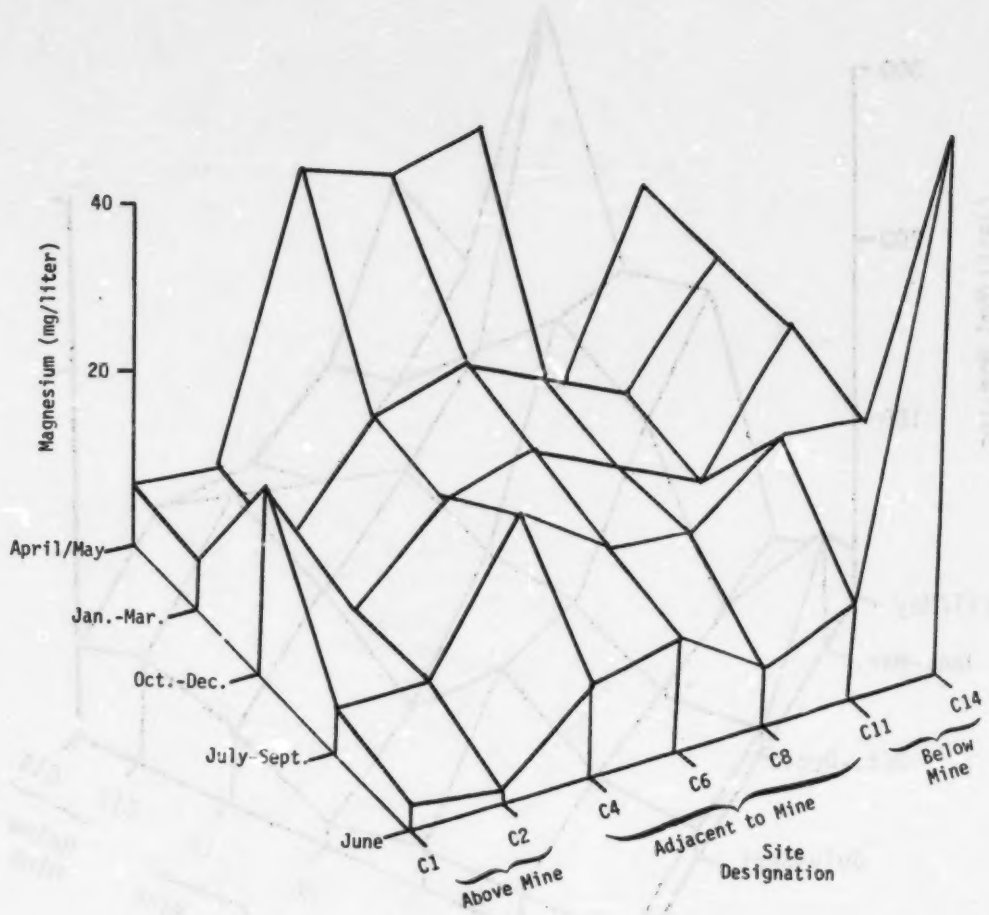

Figure 12. Spatial and temporal distribution of magnesium concentrations.

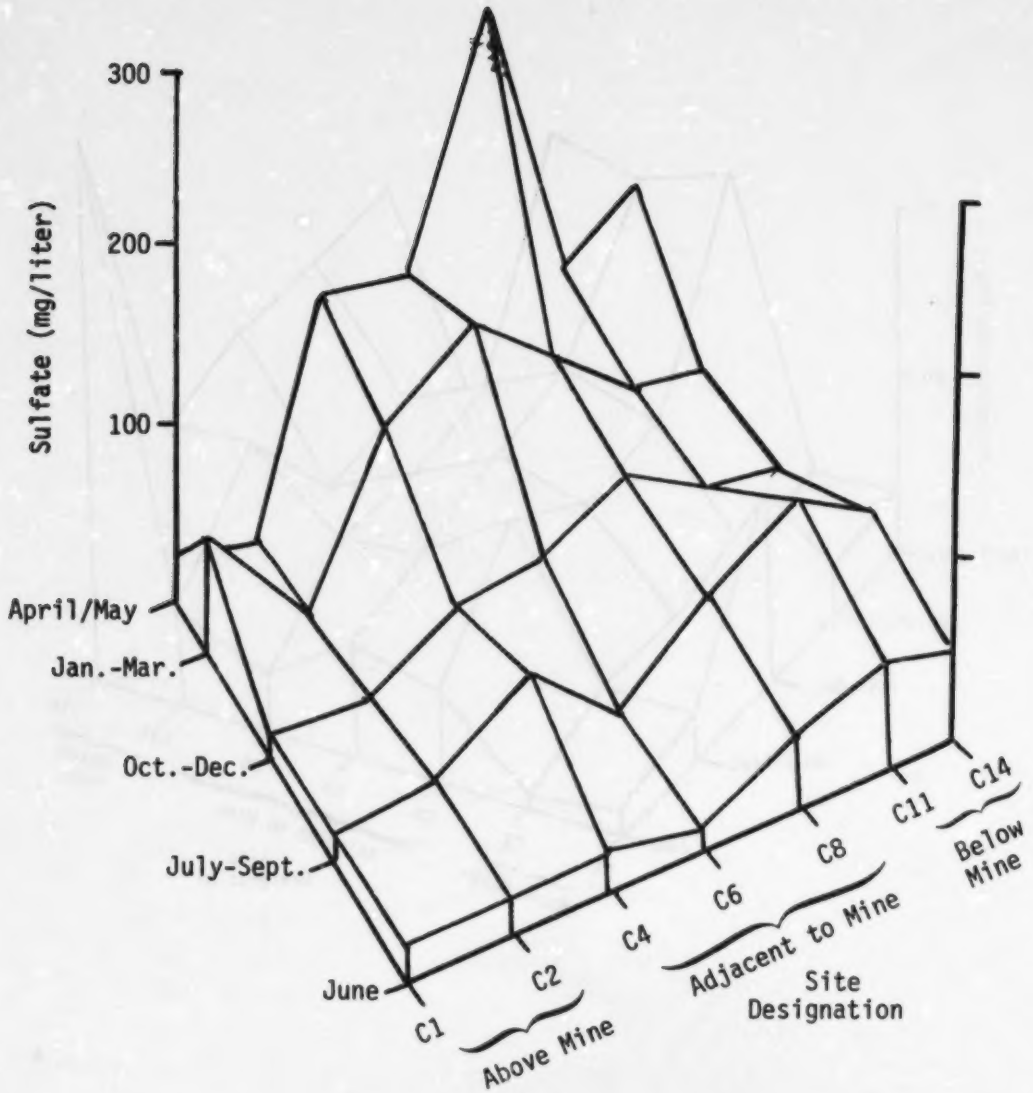

Figure 13. Spatial and temporal distribution of sulfate concentrations.

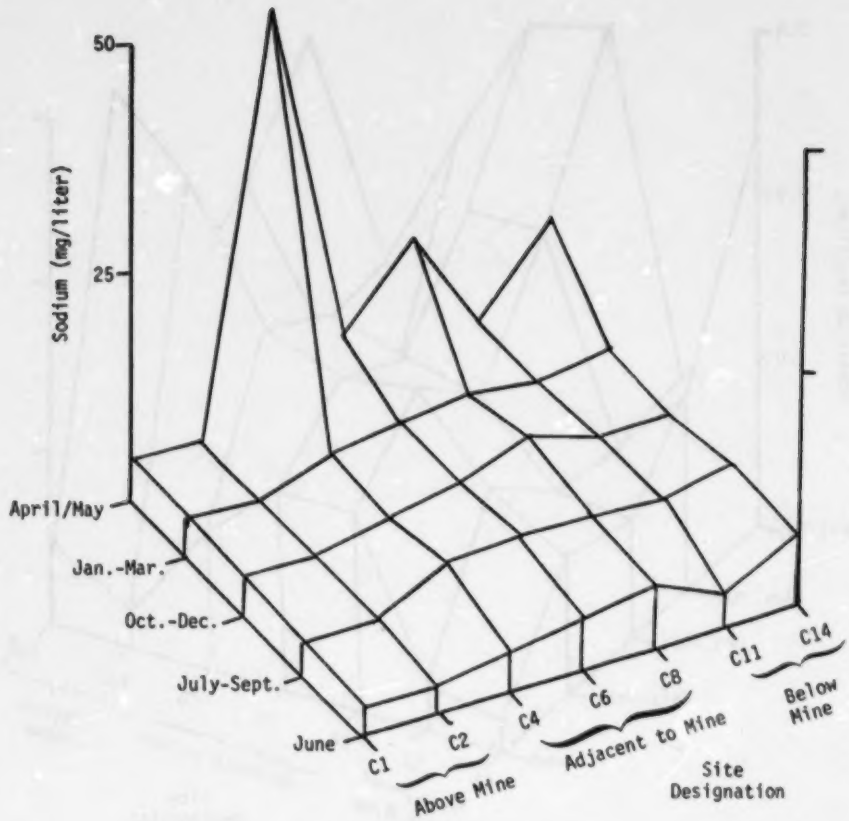

Figure 14. Spatial and temporal distribution of sodium concentrations.

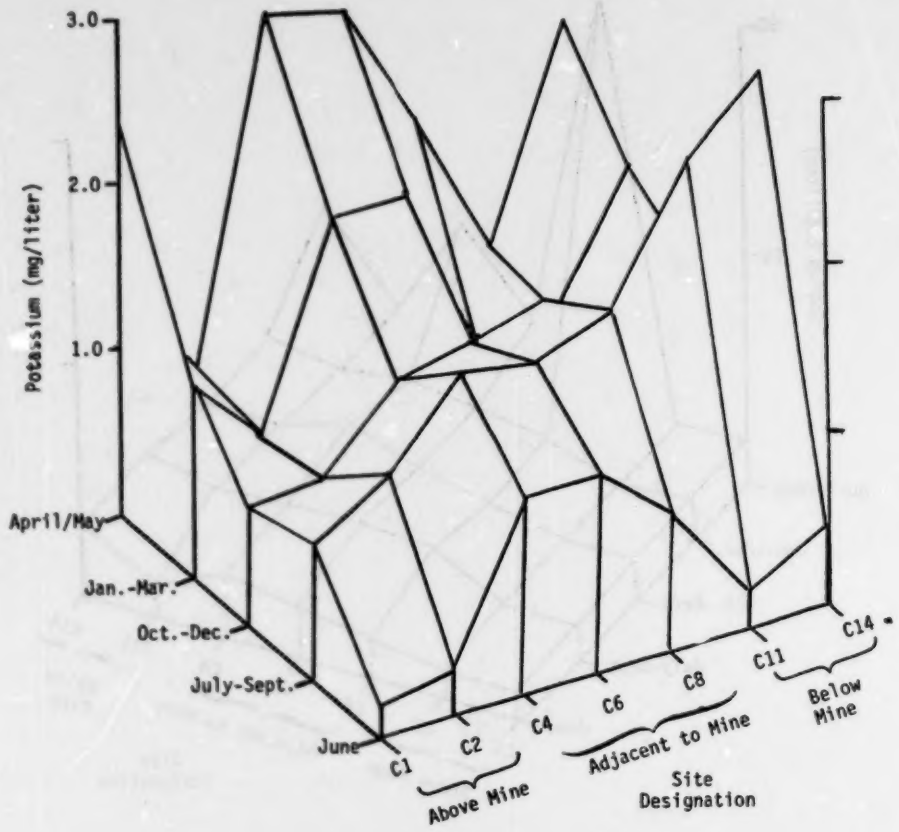

Figure 15. Spatial and temporal distribution of potassium concentrations.

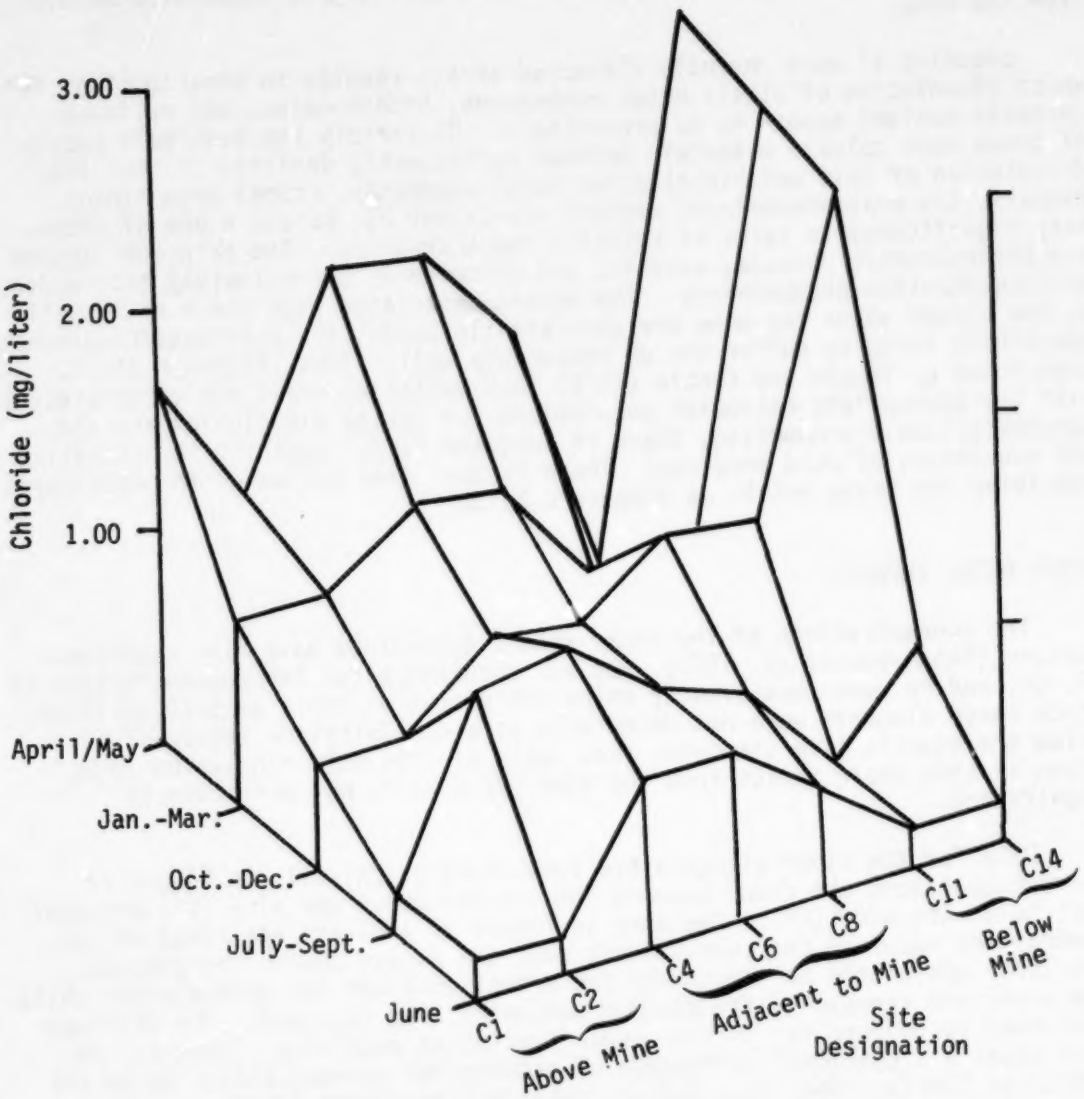

Figure 16. Spatial and temporal distribution of chloride concentrations.

These results indicate that the mine operation has a direct impact on the general water quality characteristics of Trout Creek. The principal increase in total dissolved solids is due to delivery of soluble materials from the mine.

Leaching of more recently disrupted strata results in contributions for which dissolution of alkali metal carbonates, bicarbonates, and sulfates (notably sodium) appear to be predominant. Ultimately the available supply of these more soluble materials becomes sufficiently depleted so that the dissolution of less soluble alkaline earth compounds becomes predominant. Overall, the most predominant cations are Ca and Mg; Na and K are of secondary significance in terms of relative concentrations. The principal anions are bicarbonate/carbonate, sulfate, and chloride in approximately that order of concentration predominance. The waters associated with the mine as well as the stream above the mine are consistently basic; the carbonate/bicarbonate equilibria serve to buffer the pH reasonably well. Thus, although it has been shown by Temple and Kimble (1976) that pyrite minerals are often present with the appropriate microbial populations for pyrite dissolution and the concomitant acid production, there is adequate buffer capacity to neutralize the quantities of acid produced. These factors also influence the equilibria involving the heavy metals as discussed below.

HEAVY METAL IMPACTS

The concentrations of the heavy metals determined have also been summarized (Skogerboe *et al.* 1978). At all sampling sites the concentrations of Al, Cr, and Pb were consistently below the detection limit of 5-10 µg/liter. Since these elements were not detectable at a concentration factor of 10 below the aquatic life standards (see Table 4), the only conclusion to be drawn is that their impact from the mine (if any) is not particularly significant.

Data for the other elements are summarized graphically in Figure 17 where comparisons are drawn between the station above the mine (C2) and that just below the mine (C8). The bars in Figure 17 indicate the range of concentrations observed for each element over the 2-year monitoring program. The lower end of the bar indicates the detection limit for each element while the upper end represents the maximum concentrations observed. The data were also used to compute the average concentration at each site. However, in most cases a significant percentage of samples had concentrations below the detection limits. When this was the case, the detection limit was taken as the estimate of the actual concentration present even though it was lower. As a result, the averages determined are actually upper limit estimates of the actual values; these averages are indicated by the - - symbol on each bar graph. The percentage value given at the top of each bar indicates the percentage of samples for which the element concentration was above the indicated detection limit. It should be emphasized that an average determined on the basis of detectable concentrations in only 30% of the samples (for example) will consequently be a greater overestimation of the actual value than one determined from concentrations determined in a progressively

TABLE 4. EQUILIBRIA AND EQUILIBRIUM CONSTANTS CONSIDERED IN MODEL CALCULATIONS (SILLEN AND MARTELL 1964)

Species	Product(s)	log K
H_2O	$H^+ + OH^-$	-14
H_2CO_3 (a)	$H^+ + HCO_3^-$	-6.35
	$H^+ + CO_3^{2-}$	-10.34
	$CaHCO_3^+$	1.26
	$CaCO_3^0$ a/	3.2
H_2SO_4	$H^+ + SO_4^{2-}$	-1.99
	$CaSO_4^0$	2.31
H_3PO_4	$H^+ + H_2PO_4^-$	-2.16
	$H^+ + HPO_4^{2-}$	-7.21
	$H^+ + PO_4^{3-}$	-12.33
Al(III)	$Al(OH)_3$	-32.5
	$AlPO_4$	-18.24
	$AlOH^{2+}$	9.76
	$Al(OH)_2^+$	19.4
	$Al(OH)_4^-$	28.3
	$AlSO_4^+$	3.2
	$Al(SO_4)_2^-$	5.1
Cd(II)	$CdCO_3$	-13.74
	$Cd(OH)_{1.5}(SO_4)_{0.25}$	-12.5
	$1/3\ Cd_3(PO_4)_2$	-10.72
	$CdSO_4$	-7.8
	$Cd(OH)_2$	-14.5
	$CdOH^+$	6.08

TABLE 4. CONTINUED

Species	Product(s)	log K
Cd(II) (cont.)	$Cd(OH)_2^0$	8.7
	$Cd(OH)^-$	8.38
	$Cd(OH)_4^{2-}$	8.42
	$CdSO_4^0$	2.3
	$CdCl^+$	1.95
	$CdCl_2^0$	2.5
	$CdCl_3^-$	2.35
	$CdCl_4^{2-}$	1.65
Cu(II)	$Cu(OH)_2$	-19.7
	$CuCO_3$	-9.63
	$1/3\ Cu_3(PO_4)_2$	-12.3
	$CuOH^+$	6.66
	$Cu(OH)_2^0$	14.32
	$Cu(OH)_3^-$	15.5
	$Cu(OH)_4^{2-}$	13.8
	$1/2\ Cu_2(OH)_2^{2+}$	5.26
	$CuCO_3^0$	6.34
	$Cu(CO_3)_2^{2-}$	10.01
	$CuCO_3OH^-$	15.0
	$CuSO_4^0$	2.35
	$CuCl^+$	0.95
$Hg_2(II)$	Hg_2CO_3	-16.05
	Hg_2HPO_4	-12.4

TABLE 4. CONTINUED

Species	Product(s)	log K
Hg_2(II) (cont.)	Hg_2Cl_2	-17.88
	Hg_2SO_4	-6.17
	$Hg_2SO_4^0$	1.3
	$Hg_2(SO_4)_2^{2-}$	2.4
Hg(II)	$Hg(OH)_2$	-25.4
	$HgOH^+$	10.2
	$Hg(OH)_2^0$	22.66
	$Hg(OH)_3^-$	21.8
	$Hg(OH)_4^{2-}$	21.3
	$HgSO_4^0$	1.34
	$Hg(SO_4)_2^{2-}$	2.44
	$HgCl^+$	6.74
	$HgCl_2^0$	13.22
	$HgCl_3^-$	13.79
	$HgCl_4^{2-}$	15.25
Mn(II)	$Mn(OH)_2$	-12.8
	$MnCO_3$	-9.3
	$MnOH^+$	3.41
	$Mn(OH)_3^-$	1.8
	$MnHCO_3^-$	1.8
	$MnSO_4^0$	2.26
Pb(II)	$Pb(OH)_2$	-18.7
	$PbCO_3$	-13.4

TABLE 4. CONTINUED

Species	Product(s)	log K
Pb(II) (cont.)	1/3 $Pb_3(PO_4)_2$	-14.03
	$PbHPO_4$	-9.9
	$PbCl_2$	-4.76
	$PbSO_4$	-7.8
	$PbOH^+$	6.22
	$Pb(OH)_2^0$	10.34
	$Pb(OH)_3^-$	13.95
	Pb_2OH^{3+}	6.7
	$Pb_4(OH)_4^{4+}$	35.7
	$PbCl^+$	1.6
	$PbCl_2^0$	1.78
	$PbCl_3^-$	1.68
	$PbCl_4^{2-}$	1.38
	$PbSO_4^0$	2.46
Zn(II)	$Zn(OH)_2$	-15.7
	$ZnCO_3$	-10.8
	1/3 $Zn_3(PO_4)_2$	-10.68
	$ZnOH^+$	5.04
	$Zn(OH)_3^-$	14.2
	$Zn(OH)_4^{2-}$	15.0
	$ZnSO_4^0$	2.26
	$ZnCl^+$	0.43

TABLE 4. CONTINUED

Species	Product(s)	log K
Zn(II) (cont.)	$ZnCl_2^0$	0.61
	$ZnCl_3^-$	0.53
	$ZnCl_4^{2-}$	0.2
Fe(II)	$Fe(OH)_2$	-15.1
	$FeCO_3$	-10.6
	$FeOH^+$	5.7
	$Fe(OH)_3^-$	10.0
	$Fe(OH)_4^{2-}$	9.6
Fe(III)	$Fe(OH)_3$	-38.6
	$FePO_4$	-30.02
	$Fe(OH)H_2PO_4$	-34.56
	$FeOH^{2+}$	11.81
	$Fe(OH)_2^+$	20.84
	$Fe_2(OH)_2$	24.54
	$FeSO_4^+$	4.10
	$FeCl^{2+}$	1.48
	$Fe(SO_4)_2^-$	5.44

a/ Superscript 0 indicates the compound in soluble form.

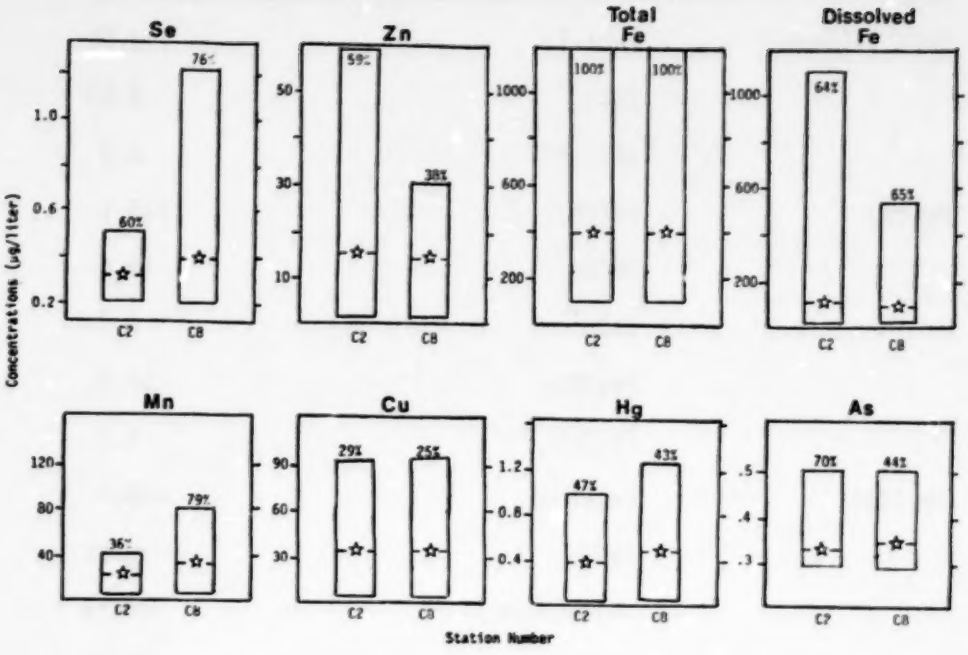

Figure 17. Elemental detection limits, observed concentration ranges, frequency of occurrence above detection limits, and average concentrations in surface waters above and below the Edna Mine. Lower limits of bars indicate detection limit; upper limits of bars indicate maximum observed concentration; ☆ indicates average concentration observed; and percentage number indicates frequency of occurrence above detection limit.

larger percentage of the samples. Nevertheless, the data can be used to draw the following inferences. A similar data summary for the subsurface water sampling sites within the mine is given in Figure 18. This also aids in the following evaluation.

Manganese

The estimated average concentration of Mn in the stream after inflow from the mine is approximately 65% higher than that above the mine. The fact, however, that Mn was detected above the mine in only 36% of the samples while 79% of those below had measurable concentrations tends to reduce the actual magnitude of difference. It is probable that a more reliable estimate of the differences could be based on multiplication of the average in each case by the frequency of observation. Thus, for Mn, the weighted averages would be 0.36(21) = 7.6 µg/liter at C2 and 0.79(31) = 24 µg/liter at C8. Using these weighted values results in an indication that the Mn concentration increases by more than 200% between C2 and C8. Although a weighting evaluation of this type can be supported on a statistical basis, it must be considered qualitative or semiquantitative at best. The fact remains, however, that Mn concentrations increase between the stations above and below the mine. Moreover, examination of the data in Figure 18 (Skogerboe *et al.* 1978) indicates that the major influx is associated with the older section of the mine (C3). This may be due to the greater infiltration of water into these spoils or to the fact that these spoils have been weathered to the extent that the controlling equilibria are shifting. The Mn concentration in groundwater in the mine at C3 exceeds the permissible level (see Table 5) of 100 µg/liter for 57% of the sample collections; this level was never exceeded in those collections made at C8 on the stream below the mine.

Copper

This element was measurable in 25-30% of all stream samples (Figure 17). Evaluation of the data generally suggests that inflow from the mine is not significant or minimal. Again it may be noted that the highest groundwater levels are associated with the older mine areas (C3, Figure 18).

Mercury

The detection of mercury in a fairly high percentage of the subsurface drainage samples in the mine (Figure 18) indicates the presence of mercury compounds or minerals that can be dissolved. The stream water analyses (Figure 17) imply the inflow of a small amount of mercury from the mine, but, on the average, this is not a particularly large contribution. The primary mercury inflow is associated with the snowmelt flushing period at the mine. Although samples have been analyzed for the presence of organo-mercury compounds, none have been detected.

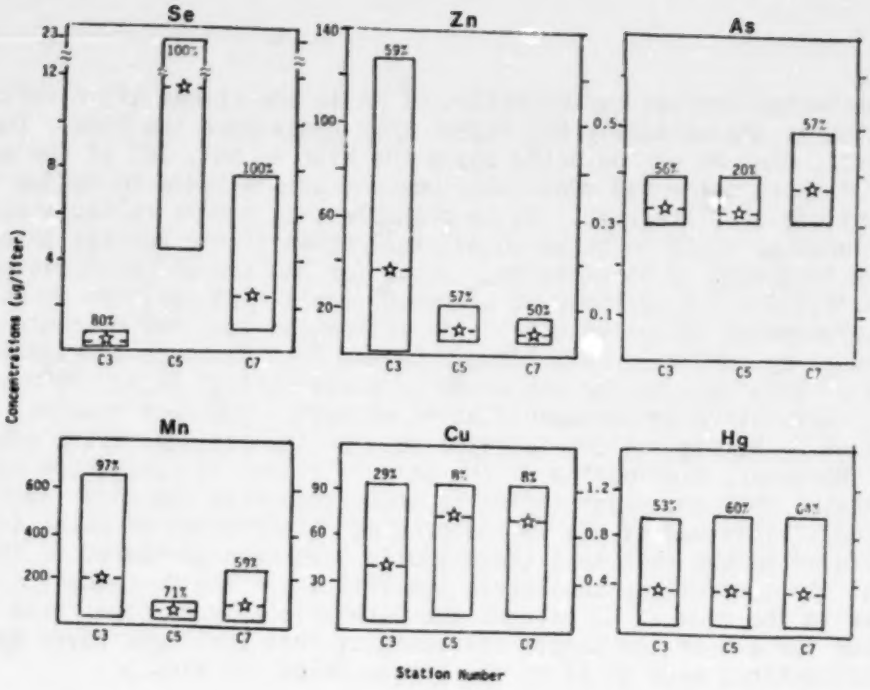

Figure 18. Elemental detection limits, observed concentration ranges, frequency of occurrence above detection limits, and average concentrations of subsurface waters in the Edna Mine. Lower limits of bars indicate detection limit; upper limits of bars indicate maximum observed concentration; ☆ indicates average concentration observed; and percentage number indicates frequency of occurrence above detection limit.

TABLE 5. QUALITY CRITERIA FOR WATER (U.S. ENVIRONMENTAL PROTECTION AGENCY, 1976)

Parameter	Aquatic life	Drinking water
Alkalinity	20 mg/liter (or more as $CaCO_3$)	--
Arsenic	100 µg/liter	50 µg/liter
Cadmium	0.4 µg/liter (soft water)[a/] 1.2 µg/liter (hard water)	10 µg/liter
Chlorine	20 µg/liter	--
Chromium	100 µg/liter	50 µg/liter
Copper	0.1 × a 96-h LC_{50}[b/] (LD_{50} 48-60 ppb)[c/]	1.0 mg/liter
Hardness	Related to what contributes to the hardness	
Iron	1.0 mg/liter	0.3 mg/liter
Lead	0.01 × a 96-h LC_{50} (LD_{50} 48-450 ppb)	50 µg/liter
Manganese	100 µg/liter	50 µg/liter
Mercury	0.05 µg/liter	2.0 µg/liter
Nickel	0.01 × a 96-h LC_{50} (LD_{50} 48-1.12 ppm)	--
Dissolved oxygen	5.0 mg/liter minimum	--
pH	6.5 to 9.0	5.0 - 9.0
Selenium	0.01 × a 96-h LC_{50}	10 µg/liter
Silver	0.01 × a 96-h LC_{50}	50 µg/liter

[a/] Soft water: 0-75 mg/liter $CaCO_3$; hard water: 150-300 mg/liter $CaCO_3$

[b/] LC_{50} is defined as the concentration of a toxicant which is lethal to 50% of the organisms tested under the test conditions in a specified time. (The receiving or comparable water should be used as the diluent for sensitive freshwater resident species.)

[c/] LD_{50} is defined as the dose of a toxicant that is lethal to 50% of the organisms tested under the test conditions in a specified time. A dose is the quantity actually administered to the organism and is not identical with a concentration, which is the amount of toxicant in a unit of test medium rather than the amount ingested by or administered to the organism [example LD_{50} 48 (number of hours) - 60 ppb].

Selenium

The data for selenium are more striking. At the off-stream sites draining the 1950 and 1960-1970 age spoils (C5 and C7, Figure 18), the observed levels are quite high and exceed those observed at the on-stream sites (Figure 17) by factors of 5 to 10. Station C5 receives water passing through an unfilled box cut in the mine. The Se level here is particularly high; the permissible level (Turbak *et al.* 1976) of 10 µg/liter was exceeded in 60% of the samples analyzed. Relatively large amounts of Se are also being leached from the newer area of the mine (C7). Clearly, larger amounts of Se are being leached from the spoils than from undisturbed strata. The distinguishing features of the C5 and C7 watersheds which account for this have not been identified. Inflow from these areas accounts for the approximately 30% to 40% average increase in the Se concentration in Trout Creek between the up- and downstream sampling sites. Again, the primary impact is observed in the spring runoff period. Checks have failed to indicate the presence of organo-selenium for these monitoring stations.

Zinc

Again, the occurrence of higher zinc concentrations in groundwater is most prominently associated with older areas of the mine (Figure 18). Consideration of the summary in Figure 17, however, indicates that the frequency of occurrence of measurable zinc is less downstream of the mine, i.e., the weighted average zinc concentration decreases. This implies that other constituents delivered to the stream from the mine suppress the concentrations of soluble zinc, e.g., by precipitation. This possibility is discussed in more depth in a section dealing with chemical equilibria below.

Arsenic

The data for this element do not parallel those for selenium. The amounts of As associated with groundwaters are relatively constant regardless of the degree of weathering of the spoils (Figure 18). Moreover, the stream data (Figure 17) again imply that other chemical contaminants from the mine may reduce the amount of soluble arsenic in the stream via some removal mechanism. It has been established that more than 95% of the As determined is inorganic; no organo-arsenic has been detected.

Iron

This element was detectable in all samples collected. Its average level in the oldest mine area (C3) was 450 µg/liter, dropping to 200 µg/liter in the C5 watershed, and rising to 1600 µg/liter in the newest area of the mine (C7). Thus, recently exposed strata contribute more iron to the groundwater than those which have undergone weathering. The average concentration in the stream remained constant, between the above- and below-mine sites, at ~400 µg/liter. Thus, although this exceeds the permissible drinking water

recommendation of 300 µg/liter, the data do not indicate input of a significant amount of iron from the mine. Again, it should be emphasized that iron minerals, including pyrite, are present but the prevalent chemical equilibria control the dissolved iron concentrations as well as neutralize any acid production due to pyrite dissolution.

SUMMARY

The heavy metal results discussed above and summarized in Skogerboe *et al.* (1978) indicate the following.

1. The mine operation has no detectable impact on Trout Creek in terms of increasing the concentrations of Al, As, Cd, Cr, Cu, Fe, Pb, or Zn.

2. Significant increases in the stream concentrations of Mn and Se due to the mine inflow can be inferred from the data. Although these increases occur, their magnitudes are such that significance in terms of potential impacts on aquatic biota does not appear likely. Exception to this may occur in the mine pond at station C5.

3. In terms of the groundwater impacts, higher concentrations of the elements Mn and Zn are associated with subsurface waters in equilibrium with the oldest spoils. The reverse appears true for Cu, Cr, and Cd but the data are much more limited. Higher levels of As, Fe, and Se are associated with groundwater in equilibrium with the less weathered spoils.

4. These general observations emphasize that the potential impacts on the surface and subsurface water quality depend on several factors including: the degree of infiltration as influenced by the mine contours and precipitation, the physical and mineralogical characteristics of the disrupted strata, the flushing (contact) time associated with the individual watersheds, the extent of spoils weathering, the oxygen availability, and the chemical equilibria operative. All these factors must be considered in predicting impacts, in evaluating the mechanistic parameters which may control these impacts, and in making recommendations for control strategies where appropriate.

SECTION VII

EVALUATION OF CHEMICAL EQUILIBRIA

As previously indicated, the primary contaminants entering Trout Creek from mine inflow are the gross water quality constituents: alkalinity and soluble salts. McWhorter *et al.* (1975) have discussed the impacts associated with these and have formulated a model offering a predictive capability. Their results are consequently not repeated here; a complete discussion is contained in their publication (McWhorter *et al.* 1975).

It has been noted above that concentrations of most heavy metals are generally in the low µg/liter range; it appears that these levels (except for As, Cd, and Hg) would not normally be considered acutely toxic to aquatic organisms. This observation is generally contrary to what has often been reported for coal development areas in the Appalachian region. Moreover, it has been noted that some heavy metals associated with energy development sites in the West occur in mineral forms normally considered soluble. Thus, it is appropriate to consider what factors may account for the low concentrations generally observed.

Fairly comprehensive water quality data sets have been accumulated for the study site described above. The data on this and other western streams are augmented by data from the respective state water resources agencies, USGS, and EPA. Examination of these data, as well as those for other streams in the western energy development area, indicates that their general water quality characteristics are quite similar on a broad scale. Based on this examination, the following generalizations can be made concerning on-stream sites at Trout Creek and numerous other western streams:

1. The observed pH values range from 6.5 to 9.5 with 93% of all values falling in the range between 7.0 and 8.5.

2. Total alkalinity ranges from 20 to 200 mg/liter (as calcium carbonate) with 85% of all values ranging between 60 and 180 mg/liter. Acidity is usually less than 1 mg/liter.

3. Total hardness ranges from 40 to 670 mg/liter as calcium carbonate, with 84% of all values falling below 250 mg/liter.

4. Total sulfate covers the 1 to 500 mg/liter range with values less than 100 mg/liter being most common.

5. Chloride concentrations rarely exceed 1 mg/liter.

6. Nitrate concentrations rarely exceed 1 mg/liter.

7. Orthophosphate levels are typically less than 0.1 mg/liter.

These parameters may be generally considered primary in controlling the chemical equilibria which determine the solubilities of many heavy metals.

In view of the mineralogical and/or chemical characteristics of the soils, sediments, and mine overburden/spoils of this region, the general concentration levels of the anionic species cited above should be essentially "fixed" in the ranges mentioned above. Moreover, the morphologies of most western streams are such that their waters will remain in reasonable equilibrium with atmospheric constituents such as CO_2 and O_2 as influenced by other parameters such as pH, temperature, alkalinity, etc. Simply stated, the observed ranges of pH, carbonate, alkalinity, sulfate, etc., can be defined as generally representative of the entire western coal development region. These ranges can consequently be taken as boundary conditions in considering the heavy metal equilibria that should prevail in the *absence* of unusual circumstances, e.g., the presence of appreciable concentrations of organic ligands. The ranges above should, within limits, be relatively unperturbed by the addition of other constituents such as metal ions unless such additions involve *major* influxes. Consequently, the equilibrium models can be used for predicting the fates of heavy metals which may be available in forms soluble under other conditions.

Equilibrium calculations can thus be used to estimate *maximum solubilities* of several heavy metals under the conditions representative of the chemical and mineralogical features of the soils and spoils and the groundwater and surface water of the area; this assumes the absence of other interacting components such as organic ligands. These calculations may be made assuming that the heavy metals in question exist in soluble forms at their origin, e.g., a strip coal mine. If they do not, the maximum solubility calculations will be overestimates of the actual case. It can be easily argued that such definitions of upper limits serve as valuable reference points.

Two general types of chemical interactions may occur for a particular metal ion and any combination of the anionic species stipulated in the above set of generalizations. Immobilization of the metal ion due to precipitation or to ion exchange type processes may occur. Alternatively, the ion may be mobilized by complexation reactions which effectively enhance its solubility. In either case, the interactions involved can be described by thermodynamic parameters. The relative significance levels of the possible equilibria can therefore be assessed on the basis of thermodynamic stabilities. Reactions resulting in the largest increases in stability will tend to be principal among the various possibilities. The compilation of equilibrium constants (Sillen and Martell 1964) has been used as the data source for the present calculations.

The equilibria considered for each metal ion are listed in Table 4. Precipitates of a complex nature [e.g., $Zn(CO_3)_{0.36}(OH)_{1.28}$] were not

considered since such precipitates are usually formed only slowly from simpler precipitates (e.g., $ZnCO_3$) rather than directly in solution. They will, therefore, not be the controlling equilibria on the time scale of importance herein, i.e., a few days. Some other equilibria could also have been included, but were rejected either because: (1) their equilibrium constants were too low to be considered significant relative to those listed, or (2) the concentrations of the anions involved indicated a lack of significance. The equilibria in Table 4 have been written so the stoichiometric coefficient of the aquated metal ion is unity. This practice has been followed to simplify model calculations. The equilibrium constants used in the calculations are also given in Table 4; values chosen were for 25°C and zero ionic strength. In instances for which two or more independent determinations of an equilibrium constant did not agree, average values were selected for the present calculations. For metals having more than one common oxidation state, all states were considered because the redox characteristics of the waters may vary significantly. In all calculations, the pH was selected as the independent (master) variable. The common ranges for each of the anions present, as indicated above, were used to define the boundary conditions for the calculations. Thus, the low and high ends of the typical concentration range for each anion were used in the calculations to define the extremes of the controlling equilibria possibilities. For anions that could be present in various forms, the pH-based calculations were used to determine the relative concentrations of each form. Carbonate, for example, may be present as dissolved CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, $CaHCO_3^+$, and $CaCO_3^0$. The species $CaHCO_3^+$ and $CaCO_3^0$ are soluble complexes which, because of the typically high levels of calcium in solution ($\geq$60 mg/liter) may tie up a significant fraction of the total carbonate. The appropriate equilibrium constants were consequently used in the calculation format outlined below to determine the respective concentrations of each of the free carbonate species at the pH level in question. The carbonate boundary condition concentrations, given as a footnote to Table 6, are thus for the total of all carbonate-related species. Similar adjustments were made for other anions as required.

Since the interest is in obtained estimates of the maximum concentration of soluble metal, any effect which will tend to increase solubility should be taken into account. The effect of ionic strength is such that solubilities of metal salts will be increased at higher ionic strength; hence a correction for ionic strength has been made; i.e., the equilibrium calculations are carried out in terms of activities which are related to concentrations by the relation:

$$a = \gamma C$$

The activity coefficient γ decreases with increasing ionic strength, where ionic strength, I, is defined by

$$I = \tfrac{1}{2} \sum_i C_i z_i^2$$

TABLE 6. COMPARISON OF CALCULATED AND OBSERVED MAXIMUM CONCENTRATIONS AT STREAM AND MINE SPOIL DRAINAGE SITES

Metal	Stream concentrations (µg/liter)		Mine spoil concentrations (µg/liter)	
	Calculated[a] maximum	Observed maximum	Calculated[b] maximum	Observed maximum
Cd(II)	3.1	1.8	2.4	10
Hg(II)	360,000	1.3	360,000	1
Al(III)	23	<500	26	<500
Zn(II)	1600	170	1500	130
Cu(II)	830	41	1400	58
Fe(III)	0.001	1100	0.001	1200
Mn(II)	45,000	180	43,000	1200
Pb(II)	14	28	14	<5

[a] Conditions: pH = 7; alkalinity = 150 mg $CaCO_3$/liter; SO_4^{2-} = 80 mg/liter; Cl^- = 1 mg/liter; PO_4^{3-} = 0.01 mg/liter.

[b] Conditions: pH = 7; alkalinity = 370 mg $CaCO_3$/liter; SO_4^{2-} = 1500 mg/liter; Cl^- = 2 mg/liter; PO_4^{3-} = 0.01 mg/liter.

where z_i is the charge of the ith ionic species and C_i is its molar concentration. The activity coefficients have been calculated for the typical concentration ranges cited above via the equation:

$$\log \gamma_{\pm z} = -A\, z^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \qquad (1)$$

where A is a constant whose value depends only on the solvent and temperature. This equation is generally accepted as the best available for estimating the values of γ in an aqueous system containing more than one salt (i.e., a mixed electrolyte system) (Stumm and Morgan 1970). Failure to include an ionic strength correction lowers the calculated total metal solubilities by 5-10% for typical stream conditions and by 5-30% for typical mine spoil drainage conditions.

As indicated above, reactions between metal ions and anions may involve precipitation or complexation. The general expression for precipitation of a metal ion, M^{n+}, by an anion, A^{m-}, is:

$$M^{n+} + n/m\, A^{m-} \rightleftarrows 1/m\, M_m A_n \qquad (2)$$

and

$$K_{sp} = (M^{n+})(A^{m-})^{n/m} \qquad (3)$$

where parentheses indicate the *activities* of the species. A similar expression for complexation would be:

$$M^{n+} + qA^{m-} \rightleftarrows MA_1^{+n-(qm)} \qquad (4)$$

and

$$K_1 = \frac{(MA_q^{n-qm})}{(M^{+n})(A^{-m})^q} \qquad (5)$$

Considering the equilibria for Zn^{2+} as an example (Table 4) the following expressions may be evaluated.

$$(Zn^{2+}) = 10^{-15.7}/(OH^-)^2 \qquad (6)$$

$$(Zn^{2+}) = 10^{-10.8}/(CO_3^{2-}) \qquad (7)$$

$$(Zn^{2+}) = 10^{-14.42}/\left((CO_3^{2-})^{0.36}(OH^-)^{1.28}\right) \qquad (8)$$

$$(Zn^{2+}) = 10^{-10.68}/(PO_4^{3-})^{2/3} \quad (9)$$

and

$$(Zn^{2+}) = 10^{-13.9}/\left((SO_4^{2-})^{1/4}(OH^-)^{3/2}\right) \quad (10)$$

Thus, for example, at pH = 7; $(OH^-) = 10^{-7}$ M; $(PO_4^{3-}) = 10^{-5}$ M; and total carbonate species $(CO_3)_T = 3 \times 10^{-3}$ M; it may be determined that the solubility of Zn will be limited principally by carbonate precipitation (Equation 7) to a molarity of 10^{-5}. This calculation has consequently defined the controlling precipitate as well as the upper limit concentration of Zn^{2+}. The quantity of interest is the total soluble zinc which is the experimentally determined quantity regardless of chemical form. Again referring to Table 4, the total soluble Zn, $(Zn)_T$, may be defined as the sum of all dissolved Zn-containing species, i.e.,

$$\begin{aligned}(Zn)_T = {} & (Zn^{2+})/\gamma\pm2 + (ZnOH^+)/\gamma+1 + (Zn(OH)_3^-)/\gamma\pm1 \\ & + (Zn(OH)_4^{2-})/\gamma\pm2 + (ZnSO_4^0) + (ZnCl^+)/\gamma\pm1 \\ & + (ZnCl_2^0) + (ZnCl_3^-)/\gamma\pm1 + (ZnCl_4^{2-})/\gamma\pm2\end{aligned} \quad (11)$$

The concentrations of each of these complexes may be expressed in terms of the (Zn^{2+}), the appropriate anion concentration, and the respective equilibrium constants. Equation 11 may be reduced to:

$$\begin{aligned}(Zn)_T = (Zn^{2+}) \Big| & 1/\gamma\pm2 + 10^{5.04}(OH^-)/\gamma\pm1 + 10^{14.2}(OH^-)^3/\gamma\pm1 \\ & + 10^{15}(OH^-)^4/\gamma\pm1 + 10^{2.26}(SO_4^{2-}) + 10^{0.43}(Cl^-)/\gamma\pm1 \\ & + \ldots\ 10^{0.2}(Cl^-)^4/\gamma\pm2 \Big|\end{aligned} \quad (12)^*$$

Evaluation of this for the pH = 7 conditions listed above when $(Zn^{2+}) = 10^{-5.0}$ indicates that the total soluble Zn concentration when complexation reactions are considered may be increased to 2.4×10^{-5} M. This coincides with a concentration of ~1.6 mg/liter. These same calculation procedures have been carried out for the given sets of boundary conditions for the metals listed in relation to pH.

The results have been summarized graphically as shown in Figures 19 and 20. In each case, the precipitating form of the element which controls its

*Calculations based on this are very much upper limit estimates since it does not take into account the possible competition between the complexing ligands for binding of other metals present.

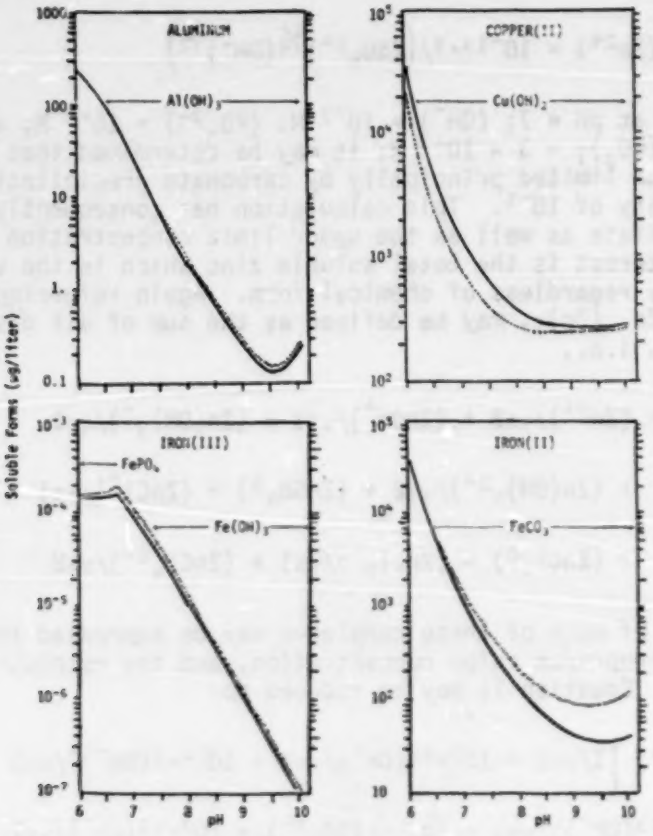

Figure 19. Solubility of metals under typical natural water conditions.

——— Conditions representative of mine spoil drainages (in mg/liter): $[HCO_3^-]$ = 450, $[SO_4^{2-}]$ = 1500 $[Cl^-]$ = 2, $[PO_4^{3-}]$ = 0.01

------ Conditions representative of on-stream conditions (in mg/liter): $[HCO_3^-]$ = 180, $[SO_4^{2-}]$ = 80, $[Cl^-]$ = 1, $[PO_4^{3-}]$ = 0.01

The precipitating forms of the element, which control the solubilities over the indicated ranges, are given on the figures.

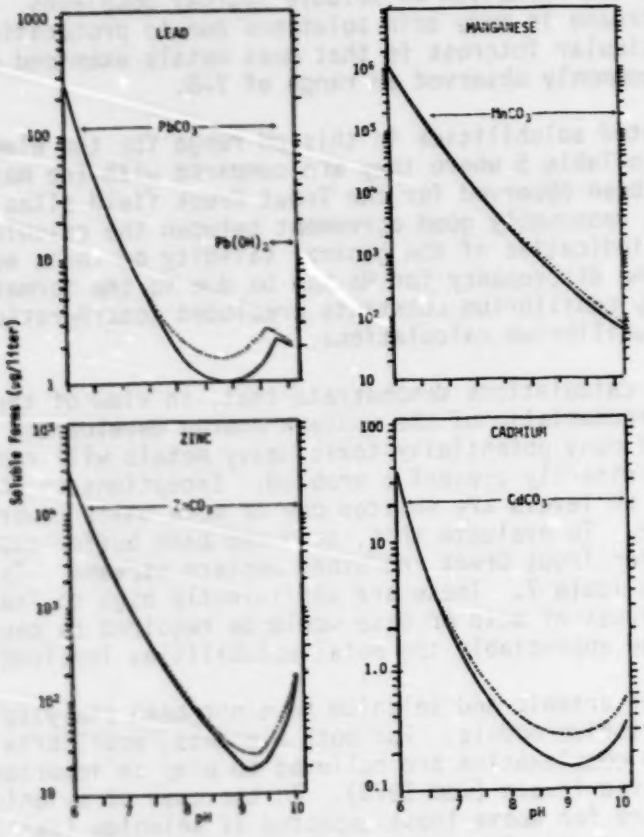

Figure 20. Solubility of metals under typical natural water conditions.

——— Conditions representative of mine spoil drainages (in mg/liter): $[HCO_3^-]$ = 450, $[SO_4^{2-}]$ = 1500, $[Cl^-]$ = 2, $[PO_4^{3-}]$ = 0.01

------ Conditions representative of on-stream conditions (in mg/liter): $[HCO_3^-]$ = 180, $[SO_4^{2-}]$ = 80, $[Cl^-]$ = 1, $[PO_4^{3-}]$ = 0.01

The precipitating forms of the element, which control the solubilities over the indicated ranges, are given on the figures.

solubility has been indicated for the applicable pH range. Examination of these results indicates that precipitation by carbonate or hydroxide are typically the controlling equilibria in this pH range. It may also be noted that the solubilities of most metals increase with pH at levels above ~8-9 due primarily to the formation of soluble hydroxy complexes. The solubilities also tend to increase in more acid solutions due to protonation of the carbonate. Of particular interest is that most metals examined are least soluble in the commonly observed pH range of 7-8.

The calculated solubilities in this pH range for the elements in question are given in Table 5 where they are compared with the maximum concentrations that have been observed for the Trout Creek field sites described previously. The reasonably good agreement between the calculated and measured values is indicative of the general validity of these equilibrium model calculations. The discrepancy for Mn may be due to the formation of MnO_2; lack of necessary equilibrium constants precluded consideration of this species in the equilibrium calculations.

These model calculations demonstrate that, in view of the typically basic waters characteristic of the western energy development areas, the soluble levels of many potentially toxic heavy metals will remain quite low and should not ordinarily present a problem. Exceptions to this may occur when the typical pH levels are shifted one or more units toward either the acid or base side. To evaluate this, acid and base buffer capacities have been calculated for Trout Creek and other western streams. Typical values are summarized in Table 7. These are sufficiently high to indicate that rather major influxes of acid or base would be required to cause a pH shift adequate to change appreciably the metal solubilities involved.

The levels of arsenic and selenium have not been analyzed in detail using these equilibrium models. For both elements, equilibria besides precipitation and complexation are believed to play an important role in determining observed levels (Hem 1970). In the case of selenium, the observed levels are far above those expected if selenide (Se^{2-}) is the oxidation state present. The selenium is probably present as either selenite (SeO_3^{2-}), or as selenate (SeO_4^{2-}). Checks have failed to indicate the presence of organo-selenium or organo-arsenic compounds. Arsenic is almost certainly present as arsenate, distributed primarily as $H_2AsO_4^-$ and $HAsO_4^{2-}$. It appears that no arsenate solubility products are exceeded in this natural water system.

Included in Table 8 is a list of the primary chemical forms in which the various metals will be present under the limiting water conditions defined above. These forms will be present regardless of whether or not the total metal can be analytically determined. Most often only one or two complexes account for most of the soluble metal and that these complexes are the aquo or hydroxo forms. In this case, the pH directly determines the exact form (aquated or hydrolyzed) of the major complex(es). For some metals (e.g., lead, manganese, and zinc) a sulfate complex may become important when sulfate levels are in large excess (>100 µg/liter); this may occur in mine spoil drainages (e.g., stations C3, C5, and C7).

TABLE 7. SUMMARY OF ACID-BASE BUFFER CAPACITIES (SKOGERBOE *ET AL.* 1978)

	Acid buffering capacity mmol/liter calculated value			Basic buffering capacities mmol/liter calculated value		
	Sites			Sites		
	4	6	8	4	6	8
Average	0.51	0.58	0.51	0.17	0.23	0.17
Standard deviation	0.26	0.48	0.33	0.05	0.13	0.08
Percent (standard deviation × 100/ave.)	51.82	82.06	64.71	29.05	56.20	47.52
Number of measurements	15.0	15.0	35.0	15.0	15.0	35.0
Minimum value	0.19	0.18	0.11	0.11	0.10	0.07
Maximum value	1.12	1.90	2.08	0.31	0.50	0.52

TABLE 8. PRIMARY CHEMICAL FORMS OF SOLUBLE METALS PREDICTED BY THE EQUILIBRIUM COMPUTATIONS

Metal	Primary metal complexes in the pH range 7-8[a,b]	
	Major forms	Secondary forms
Cu(II)	$Cu(OH)_2^0$ (37-89)	$CuOH^+$ (8.8-2)
	$CuCO_3^0$ (26-7)	$Cu(OH)_3^-$ (0.4-0.8)
	$Cu(aq)^{2+}$ (25-0.6)	$CuHCO_3^-$ (0.1-0.4)
Fe(II)	$Fe(aq)^{2+}$ (87-68)	$Fe(OH)^+$ (3.5-26)
		$FeSO_4^0$ (8-6)
Fe(III)	$Fe(OH)_2^+$ (99-100)	$FeOH^{2+}$ (1-0)
Hg(II)	$Hg(OH)_2^0$ (100)	None
Mn(II)	$Mn(aq)^{2+}$ (87-86)	$MnCO_3^0$ (5.9-6.8)
		$MnSO_4$ (7.1-6.7)
Pb(II)	$Pb(aq)^{2+}$ (79-41)	$Pb(OH)_2^0$ (0.01-0.6)
	$PbOH^+$ (10-53)	$PbSO_4$ (10-4)
Zn(II)	$Zn(aq)^{2+}$ (92-86)	$ZnOH^+$ (0.79-7.3)
		$ZnSO_4^0$ (7.4-6.7)

[a] Other conditions: alkalinity = 100 mg/liter ($CaCO_3$); sulfate = 100 mg/liter; chloride = 10^{-1} mg/liter; phosphate = 10^{-1} mg/liter; i = 0.006 M.

[b] Numbers in parentheses are the percents present in these forms in the pH range 7-8.

The equilibria for copper present a striking contrast to the other metal ions because a large fraction is present as a carbonate complex. The form of copper may also vary drastically, ranging from the aquo form under slightly acidic conditions, to the carbonate forms in waters of high carbonate alkalinity. No other metal examined shows so much variation in speciation depending upon the exact conditions.

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